Analysis and fate of combustion residues in soil

Abstract

Combustion residues from biomass and fossil fuel burning, called black carbon (BC), make up a small but very significant part of the global carbon cycle. These residues are universally found in soils, lacustrine and marine sediments and the atmosphere. They can be involved in important global processes, including carbon sequestration, pollutant binding, solar radiation reactions and can also be used to reconstruct fire histories. Black carbon does not have a defined structure, and since it represents combustion residues and condensates from various sources, it is viewed as a combustion continuum, ranging from slightly charred biomass to highly condensed soot, rather than one substance. There are a variety of methods, each quantifying a different part of the combustion continuum and overlapping in detection regions in some cases. Results from these different methods are not comparable, and therefore compiling a composite picture of BC concentrations in the environment is difficult. Reference materials analysed for BC with different methods would assist in drawing conclusions from and elucidating incomparable results. A structured means of achieving such a goal would be an intercomparative study where a number of laboratories employing different methods, all measure these reference materials for black carbon, and compare results. In this study, 12 reference materials from different environments were chosen to serve as reference materials in standardising and validating BC results from various methods. The materials are divided into three sets: (i) laboratory-produced BC-rich materials (n-hexane soot, wood char, grass char); (ii) non-BC materials that could potentially interfere with analysis (melanoidin, shale, bituminous coal, lignite coal); and (iii) environmental matrices that probably contain BC (urban aerosol, harbour marine sediment, two soils, dissolved organic matter). Char reference materials did not exist, and were specifically synthesised. They were chemically characterised, compared to other synthesised and natural chars and found to represent charcoal from typical low temperature fires. All twelve materials were used in a intercomparative study of black carbon quantification techniques, involving 17 international laboratories, employing seven different thermal and chemical oxidation methods. The results for all the materials analysed with the different methods were very disparate. Most methods quantified black carbon in the BC-rich materials, except two, whose harsh oxidation techniques oxidised all the carbon in the charcoals. Many methods found BC in the non-BC materials, thereby failing to exclude biases from these potential interfering materials. There was a large variation in concentrations of BC measured in the environmental samples. The chemical and physical properties of the materials were studied to elucidate how they influenced the BC quantification with different methods. The BC-rich materials were very similar, but the soot had a more condensed structure than the chars. The non-BC potentially interfering materials share properties with the BC-rich materials, which could lead to false positive data from non-BC materials and an overestimation of BC. The environmental matrices have relatively high amounts of inorganic matter and metal oxides, which have the potential to catalyse or inhibit thermal and chemical reactions in black carbon analysis. This study shows that any attempt to merge data generated via different methods must consider the different, operationally defined analytical windows of the BC continuum detected by each technique, as well as the limitations and potential biases of each technique. The benzene polycarboxylic acid markers method, employed in the ring trial by our laboratory, gave reasonable results for all the materials, in particular the soil matrices, for which this method was designed. We used this method in a case study to quantify the BC stock in a BC-rich steppe soil in Russia. This soil was sampled twice, 100 years apart, and we determined a BC stock loss of 25% over the whole soil profile (up to 130 cm). We used these stock values to calculate a BC turnover rate of 212-541 years for this soil, according to different assumptions, which is two to five times faster than the turnover (100 years) currently ascribed to inert carbon by the Intergovernmental Panel on Climate Change. Thus, BC in soil is not as stable as is

currently assumed. Because fossil fuel burning and vegetation fires will probably increase in future, it will be important to quantify the potential of BC as a carbon sink in soils and sediments. In the foreseeable future, BC method standardisation and calibration will be a continuing process.

Analysis and Fate of Combustion Residues in Soil

Dissertation

zur

Erlangung der naturwissenschaftlichen Doktorwürde
(Dr. sc. nat.)

vorgelegt der
Mathematisch-naturwissenschaftlichen Fakultät
der
Universität Zürich
von

Karen Hammes
aus Südafrika

Promotionskomitee:
Prof. Dr. Michael W.I. Schmidt (Vorsitz)
Dr. Ronald J. Smernik
Dr. Alexander Heim

Zürich, 2007

vir kipp

ABSTRACT

Combustion residues from biomass and fossil fuel burning, called black carbon (BC), make up a small but very significant part of the global carbon cycle. These residues are universally found in soils, lacustrine and marine sediments and the atmosphere. They can be involved in important global processes, including carbon sequestration, pollutant binding, solar radiation reactions and can also be used to reconstruct fire histories. Black carbon does not have a defined structure, and since it represents combustion residues and condensates from various sources, it is viewed as a combustion continuum, ranging from slightly charred biomass to highly condensed soot, rather than one substance.

There are a variety of methods, each quantifying a different part of the combustion continuum and overlapping in detection regions in some cases. Results from these different methods are not comparable, and therefore compiling a composite picture of BC concentrations in the environment is difficult. Reference materials analysed for BC with different methods would assist in drawing conclusions from and elucidating incomparable results. A structured means of achieving such a goal would be an intercomparative study where a number of laboratories employing different methods, all measure these reference materials for black carbon, and compare results.

In this study, 12 reference materials from different environments were chosen to serve as reference materials in standardising and validating BC results from various methods. The materials are divided into three sets: (i) laboratory-produced BC-rich materials (n-hexane soot, wood char, grass char); (ii) non-BC materials that could potentially interfere with analysis (melanoidin, shale, bituminous coal, lignite coal); and (iii) environmental matrices that probably contain BC (urban aerosol, harbour marine sediment, two soils, dissolved organic matter). Char reference materials did not exist, and were specifically synthesised. They were chemically characterised, compared to other synthesised and natural chars and found to represent charcoal from typical low temperature fires. All twelve materials were used in a intercomparative study of black carbon quantification techniques, involving 17 international laboratories, employing seven different thermal and chemical oxidation methods.

The results for all the materials analysed with the different methods were very disparate. Most methods quantified black carbon in the BC-rich materials, except two, whose harsh oxidation techniques oxidised all the carbon in the charcoals. Many methods found BC in the non-BC materials, thereby failing to exclude biases from these potential interfering materials. There was a large variation in concentrations of BC measured in the environmental samples.

The chemical and physical properties of the materials were studied to elucidate how they influenced the BC quantification with different methods. The BC-rich materials were very similar, but the soot had a more condensed structure than the chars. The non-BC potentially interfering materials share properties with the BC-rich materials, which could lead to false positive data from non-BC materials and an overestimation of BC. The environmental matrices have relatively high amounts of inorganic matter and metal oxides, which have the potential to catalyse or inhibit thermal and chemical reactions in black carbon analysis. This study shows that any attempt to merge data generated via different methods must consider the different, operationally defined analytical windows of the BC continuum detected by each technique, as well as the limitations and potential biases of each technique.

The benzene polycarboxylic acid markers method, employed in the ring trial by our laboratory, gave reasonable results for all the materials, in particular the soil matrices, for which this method was designed. We used this method in a case study to quantify the BC stock in a BC-rich steppe soil in Russia. This soil was sampled twice, 100 years apart, and we determined a BC stock loss of 25% over the whole soil profile (up to 130 cm). We used these stock values to calculate a BC turnover rate of 212-541 years for this soil, according to different assumptions, which is two to five times faster than the turnover (100 years) currently ascribed to inert carbon by the Intergovernmental Panel on Climate Change. Thus, BC in soil is not as stable as is currently assumed.

Because fossil fuel burning and vegetation fires will probably increase in future, it will be important to quantify the potential of BC as a carbon sink in soils and sediments. In the foreseeable future, BC method standardisation and calibration will be a continuing process.

ZUSAMMENFASSUNG

Verbrennungsrückstände aus Biomasse und fossilen Energieträgern werden als „Black Carbon“ (BC), zu deutsch schwarzer Kohlenstoff, bezeichnet. Sie stellen einen kleinen, jedoch sehr wichtigen Anteil des globalen Kohlenstoffkreislaufs dar. Diese Verbrennungsrückstände kommen ubiquitär in Böden, See- und Flusssedimenten sowie in der Atmosphäre vor. Sie sind in wichtige globale Prozesse wie Kohlenstoffsequestrierung, Schadstoffbindung und die Absorbtion der Soleneinstrahlung involviert und können ausserdem für die Rekonstruktion der Feuergeschichte von Landschaften verwendet werden. Black Carbon hat keine definierte chemische Struktur, es repräsentiert Verbrennungsrückstände und Kondensate aus verschiedensten Quellen. Black Carbon wird daher nicht als eine definierte Substanz angesehen, sondern als Kontinuum einer Reihe von Substanzen, die von leicht verkohlter Biomasse bis zu hoch kondensiertem Russ reicht.

Es gibt eine Vielzahl von Methoden zur Analyse dieser Verbindungen, jede davon erfasst einen anderen Bereich des Kontinuums, wobei sich diese Bereiche teilweise überlappen. Die Ergebnisse der verschiedenen Methoden sind nicht ohne weiteres vergleichbar, weshalb es sehr schwierig ist, eine umfassende Abschätzung der Konzentrationen von BC in der Umwelt vorzunehmen. Sehr nützlich für die vergleichende Interpretation der Ergebnisse von verschiedenen Methoden wäre eine gezielte Analyse der BC-Konzentrationen ausgewählter Referenzmaterialien mit den einzelnen Methoden. Eine Möglichkeit dieses Ziel zu erreichen ist ein Ringversuch, bei dem eine grosse Anzahl von Labors die verschiedenen Methoden auf unterschiedliche Referenzmaterialien anwendet und die Ergebnisse dann verglichen werden.

In der hier vorliegenden Studie wurden zwölf Referenzmaterialien unterschiedlicher Herkunft ausgewählt, um damit eine Standardisierung und Validierung der BC-Ergebnisse der verschiedenen Methoden zu erreichen. Die Materialien wurden in drei Gruppen aufgeteilt: (i) im Labor hergestellte BC-reiche Materialien, (ii) Nicht-BC-Materialien die möglicherweise die Analyse von BC beeinträchtigen können, und (iii) Umweltbestandteile, die möglicherweise BC enthalten. Referenzmaterialien für Holzkohle und verkohlte Gräser existieren nicht und wurden daher speziell hergestellt, und waren repräsentativ für Kohle aus Niedertemperatur-Feuern. Alle zwölf Materialien wurden in einem Ringversuch zu BC-Quantifizierungsmethoden getestet. Insgesamt nahmen 17 Labors teil, die sieben verschiedene Methoden anwendeten. Die Resultate für die einzelnen Materialien und Methoden erwiesen sich als grundverschieden. Mit den meisten Methoden gelang es, tatsächlich vorhandenes Black Carbon in den BC-reichen Materialien zu quantifizieren. Mit einigen Methoden konnte BC in Nicht-BC-Materialien nachgewiesen werden. Diese Methoden können somit zu falschen positiven Befunden führen. Bei den Messwerten aus Umweltproben wiederum schwankte die gemessenen BC-Konzentrationen je nach Methode. Die chemischen und physikalischen Eigenschaften der Materialien wurden untersucht, um ihren Einfluss auf die BC-Quantifizierung mit verschiedenen Methoden aufzuklären. Unter den BC-reichen Materialien war der Russ stärker kondensiert als Holzkohle, was zu unterschätzung das BC-Gehalts der Holzkohle führte. Die Nicht-BC-Materialien hatten ähnliche Eigenschaften wie die BC-reichen Materialien, was zu den falschpositiven Daten für Nicht-BC-Materialien und einer Überschätzung der BC-Konzentration führte. Naturstoffe enthalten relativ hohe Mengen anorganischer Substanzen und Metalloxide. Diese können die thermischen und chemischen Reaktionen der BC-Bestimmung katalytisieren oder behindern.

Die Benzol-Polycarbonsäure-Methode, welche im Ringversuch zur Anwendung kam, ergab sinnvolle Ergebnisse für Bodenproben, für die diese Methode auch entwickelt wurde. Wir verwendeten diese Methode in einer Fallstudie für die Quantifizierung von BC-Vorräten in BC-reichen Steppenböden in Russland. Der Boden wurde zu zwei Zeitpunkten, die etwa einhundert Jahre auseinander liegen, beprobt. Dabei wurde ein Verlust der BC-Vorräte von 25% im gesamten Bodenprofil (bis 130 cm) festgestellt. Für diesen Boden berechneten wir BC-Umsatzraten von 212 bis 541 Jahren. Der Umsatz ist in diesem Fall zwei- bis fünffach höher verglichen mit dem Wert von 1000 Jahren den das *International Panel on Climate Change* angibt, und deutet darauf ein dass BC in der Umwelt weniger stabil ist als bisher angenommen.

Da davon ausgegangen werden muss, dass Verbrennungsprozesse in Zukunft eher zunehmen werden, ist es für die Abschätzung des Kohlenstoff-senkenpotentials von BC essentiell dass es möglichst genau quantifiziert werden kann. Einer weitergehenden Standardisierung und Kalibrierung der BC-Methoden sollte daher in künftigen Arbeiten besonderes Augenmerk geschenkt werden.

CONTENTS

PART A

Introduction

"There is not better time to be studying C cycling. The global C cycle is changing, so we have a long list of tantalizing, relevant questions to puzzle, amuse, and bemuse us. And, like never before, we have a ready audience, waiting for our findings and insights. That may make us a little nervous, but at the same time it adds urgency and spice to the science. It may be, a century from now, when our work is done and the current turbulence of the C cycle has been calmed, that our successors will look back and say: it must have been an exciting time for scientists, back then, in the golden age of C cycle science."

H.H. Janzen, 2004. Agriculture, Ecosystems and Environment 104, 399-417.

THE OTHER SIDE OF GLOBAL WARMING

The evidence is indisputable – the global climate is changing, and our striving for industrial progress is to blame, including activities like fossil fuel and waste burning, and clearing of forests for agriculture by burning. Biomass fires alone affect a greater area over a wider variety of biomes than any other natural disturbance, and are contributing significantly to climate change (Lavorel et al., 2006). These activities are releasing ever more quantities of carbon dioxide (CO_2), the most important greenhouse gas, into the atmosphere (IPCC, 2007). Together with other gases and particles like methane, ozone, nitrogenous gases, and aerosols, these greenhouse gases trap radiation in the atmosphere and have resulted in a rapid increase in global warming over the last 150-200 years (Etheridge et al., 1996). If not halted, this increase in global warming will have catastrophic consequences for life on Earth as we know it: increasing sea levels due to polar ice melting, severe droughts, intensified storms, thawing permafrost, and species extinction, to name a few (IPCC, 2007).

However, not all burning achieves perfect combustion to CO_2 and H_2O. Combustion residues from biomass burning and condensates from fossil fuel burning make up a small but significant part of the global carbon cycle, constituting about 1-3% of equivalent CO_2 also produced during combustion (Druffel, 2004). The current production estimate of combustion residues is 0.05-0.26 Pg yr^{-1} (Pg = 10^{15} g), with sources including deforestation, Amazon and boreal forest burning, savanna fires, agricultural waste, fuel wood and fossil fuel burning (Kuhlbusch and Crutzen, 1995; Forbes et al., 2006). These residues can potentially play important roles in numerous biogeochemical processes, like scattering atmospheric radiation (Crutzen & Andreae, 1990; Koelmans et al., 2006), binding organic pollutants and heavy metals (Glaser et al., 2005; Gustafsson et al., 1997, Jonker et al., 2002), increasing soil carbon and fertility (Glaser et al., 2002; Schmidt et al., 2002; Skjemstad et al., 2002) and increasing the carbon concentration in sediments (Masiello & Druffel, 1998). The latter role can be interpreted as a sequestration potential to offset increases in atmospheric CO_2 (Kuhlbusch, 1995; Schmidt & Noack, 2000; Ansley et al., 2006). Black carbon can also act as a tracer for prehistoric fires (Eckmeier et al., in press).

THE GLOBAL CARBON CYCLE – THE ROLE OF COMBUSTION RESIDUES

How do these combustion residues fit into the global carbon cycle? In the global carbon (C) cycle, carbon is constantly exchanged between reservoirs on land (living biota, decaying organic matter, geological reservoirs), in the atmosphere (CO_2) and in rivers and oceans (mainly dissolved CO_2) (Fig. 1a).

Combustion residues form part of this cycle, but constitute only a fraction of the carbon globally cycled (Fig. 1b). From where combustion residues are formed *in situ* on land, they can be transported by means of soil water, surface water and air, and are universally found in soils, lacustrine and marine sediments and the atmosphere (Fig. 1b). More than 80% of the combustion residues produced are deposited on or in the soil near the site of production (Fig. 1b), where they can remain for hundreds or thousands of years in some cases (Forbes et al., 2006). For example, charcoal pieces in Brazil have been found at 50-150 cm depth, which were deposited somewhere between 3000-6000 years before present (Gouveia et al., 2002). Some soils contain up to 45% organic carbon (OC) in the form of these combustion residues (Schmidt et al., 2002). From the soil, these residues can be transported as particles via erosion or in other forms, e.g. dissolved organic carbon (DOC) to rivers, and eventually ending up in the ocean (Rumpel et al., 2006) (Fig.1b).

About 20% of combustion residues formed, end up in the atmosphere, where they can reside from days to months (Fraser & Lakshmanan, 2000; Druffel, 2004), and be transported on wind currents to rivers or the ocean (Fig. 1b).

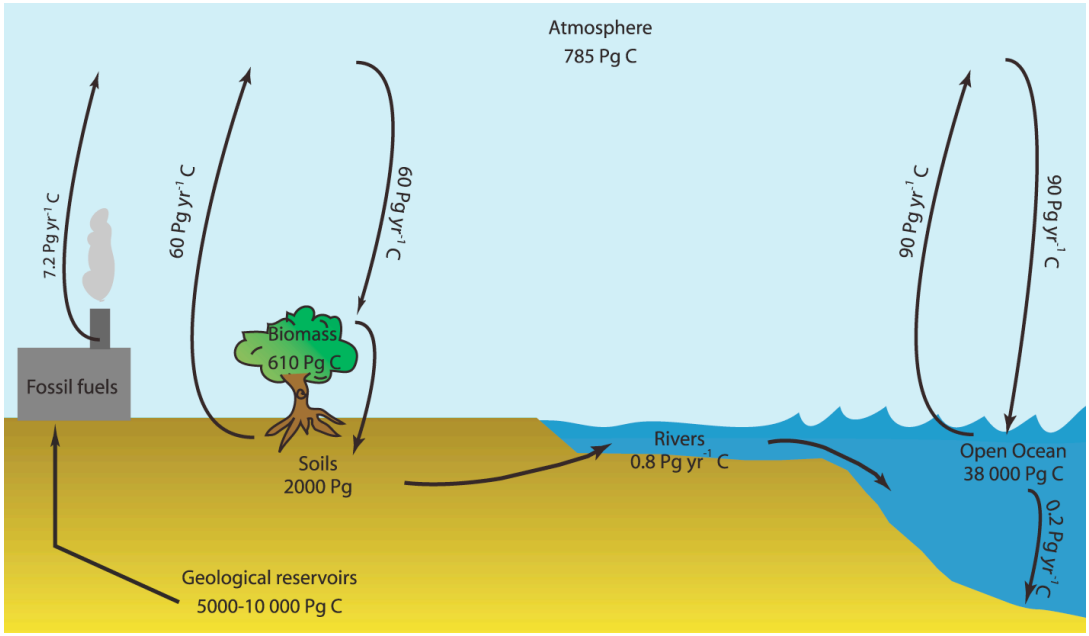

Fig. 1a. The global carbon cycle (adapted from IPCC, 2001; 2007 & Janzen, 2004)

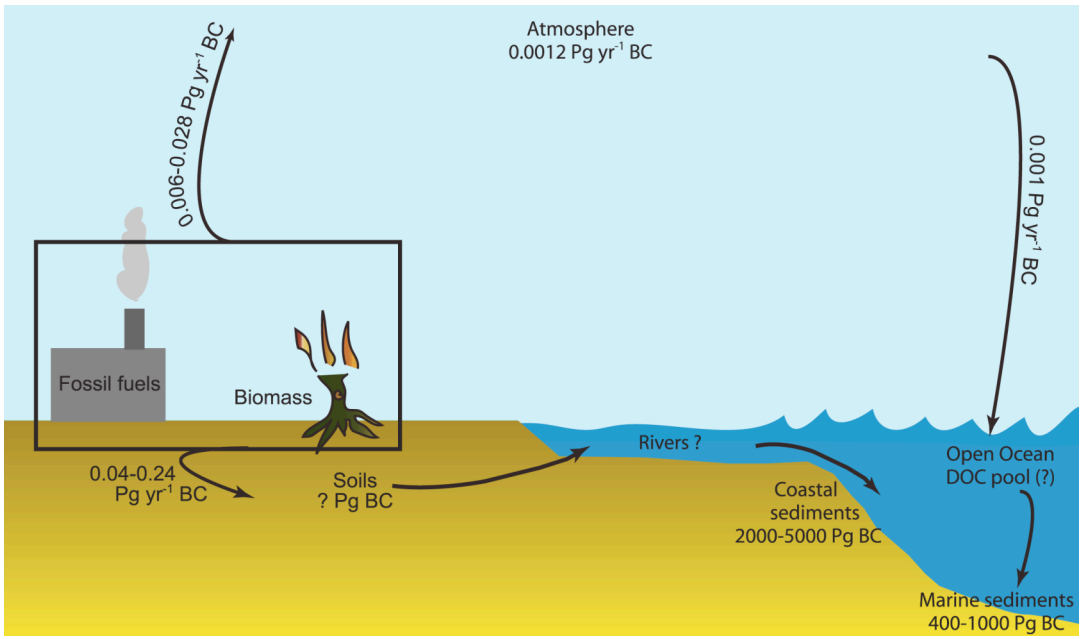

Fig. 1b. The global black carbon cycle (adapted from Masiello & Druffel, 1998 & Forbes et al., 2006)

Mitra et al. (2002) quantified particulate organic carbon (POC) in the Mississippi river, which drains a heavily industrialised area, and suggested that this river contributed 5% of all the combustion residues that were buried in the ocean a specific year (1999). The ocean is believed to be the ultimate sink for combustion residues, where these residues are 2400 to 13900 carbon-14 years[1] older than non-combusted sedimentary organic carbon deposited at the same time (Masiello & Druffel, 1998).

[1] carbon-14 years: ^{14}C is a radioactive carbon isotope. Atoms of the same atomic number but different atomic weights are called isotopes. ^{14}C has a half-life of 5730 years and is used to quantify the age of carbon up to about 60,000 years. These dates are not calibrated and are reported in radiocarbon years before present (before 1950 AD) (Killops & Killops, 2005)

DEFINING COMBUSTION RESIDUES - NOMENCLATURE

Combustion residues are viewed primarily from two perspectives: (i) the atmosphere and (ii) soils and sediments. Atmospheric scientists generally use two terms when studying combustion residues: i) black carbon (BC) and ii) elemental carbon (EC). Black carbon, as the name implies, is dark in colour (black or brown) and consists mostly of carbon (Andreae and Gelenscér, 2006). The dark colour of the material is the defining property when assessing black carbon in the atmosphere, where the origin of the material does not play a role (i.e. it does not need not be a combustion residue). The reflectance or transmittance of particles in the air (related to colour) affects solar radiation and other aspects of atmospheric chemistry. Elemental carbon, on the other hand, is operationally defined as the fraction of relatively inert carbonaceous combustion residues that is oxidised above a certain temperature threshold, in the presence of an oxygen-containing atmosphere (Andreae & Gelencsér, 2006).

In soil and sediment studies, these combustion residues are also called black carbon, but share the definition with elemental carbon (above). The term black carbon was introduced by Novakov (1984) as "combustion produced black particulate carbon having a graphitic microstructure". There has been much confusion regarding the naming of combustion residues and related materials in soils and sediments. Other definitions that have been used include: soot, smoke, carbon black, charcoal, spheroidal carbonaceous particles, graphitic carbon, charred particles (Gustafsson et al., 1997), charcoal C (Skjemstad et al., 2002), C_{pyr} – Pyrogenic carbon, black carbon, aromatic carbon of pyrogenic origin (Glaser & Amelung, 2003), PyC – the whole continuum of fire-altered biomass and organic matter (Preston and Schmidt, 2006).

In soil and sediment sciences, black carbon has in fact little to do with the black colour of the material, which is coincidental. Here, the recalcitrance of the material is one of the most important features, as well as the origin of the material, which should be fossil fuel or biomass burning residues. It is in this context that the term black carbon and abbreviation BC will be used in this thesis.

THE BLACK CARBON COMBUSTION CONTINUUM

Black carbon is heterogeneous in nature, and contains more than 60% carbon (Goldberg, 1985). Depending on the degree of condensation[2], the BC material will have a specific hydrogen/carbon (H/C) and oxygen/carbon (O/C) atomic ratio, which allows BC to be described as a *combustion continuum* rather than a specific substance (Fig. 3). This continuum encompasses combustion condensates mainly from fossil fuel burning as well as combustion residues mainly from biomass burning. Soot BC is formed in the gas phase at higher temperatures than char (>500 °C), mostly from fossil fuel burning (Akhter et al., 1985). It has a highly ordered aromatic core and a loosely structured outer surface (Schmidt & Noack, 2000) and seems to be more resistant to chemical and thermal degradation than char (Elmquist et al., 2006).

Soot particles tend to cluster immediately after formation to form compact aggregates as illustrated well in the scanning electron micrographs taken by Fernandes et al. (2003) (Fig. 4a), where they characterised several different combustion residues in terms of their environmental implications. Soot can also form from biomass burning (like chimney soot), but has a more amorphous structure than soot from fossil fuel burning (Fig. 4e).

[2] Condensation is a reaction that joins together two molecules with the elimination of a simple molecule, e.g. H_2O (Killops & Killops, 2005). In this case, the material becomes enriched in carbon.

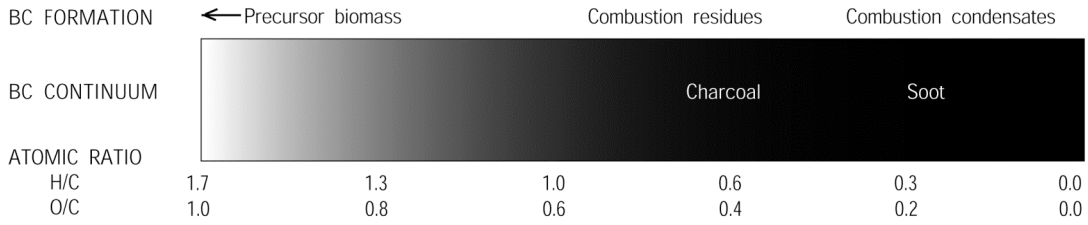

Fig. 3. Schematic presentation of the black carbon continuum (adapted from Paper 3)

Other black, carbon-rich materials have been confused with black carbon, among them "carbon black". Carbon black and soot have similar morphologies, but Watson & Valberg (2001) clearly describe the difference between the two, since carbon black is not black carbon: "Carbon blacks are manufactured under controlled conditions for commercial use primarily in the rubber, painting, and printing industries. In contrast, soots are unwanted byproducts from the combustion of carbon-based materials for the generation of energy or heat, or for the disposal of waste." Indeed, if combustion were complete, fossil fuels would burn only to CO_2.

During char formation, cellulose- or lignocellulose-rich materials are transformed into condensed aromatic ring structures that are usually loosely ordered stacks of graphene[3]-like sheets (Schmidt & Noack, 2000). The original structure of the material is often still visible (Fig. 4b & c) even after thousands of years (Smith et al., 1973, Schmidt & Noack, 2000, Fernandes et al., 2003). With increasing formation temperature, the aromaticity[4] of char BC increases, and the H/C and O/C atomic ratios decrease (Baldock & Smernik, 2000; Masiello, 2004).

Kuhlbusch & Crutzen (1995) proposed a BC-char definition where BC has a H/C atomic ratio of ≤0.2 (and be resistant to heating in oxygen at 340 °C). However, it has clearly been proven that the H/C (and O/C) atomic ratio of a charred material depends to a large extent on the formation temperature (Baldock & Smernik, 2002; Braadbaart et al., 2004), and again supports the idea of a combustion continuum rather than one substance. Nguyen et al., (2004) illustrated well that chars formed at low temperatures are less resistant to thermal degradation during black carbon analysis by certain methods, than chars and soot formed at higher temperatures.

Black carbon quantification methods could thus benefit from a set of standard materials covering a whole spectrum of BC sources and matrices, including charcoals (Schmidt et al., 2003). These charcoals, produced under known conditions and chemically characterised, would represent natural charcoals as reference materials for calibration of quantification methods.

BLACK CARBON QUANTIFICATION

There are six major methods for quantifying BC in soils and sediments and one most often used to quantify BC in aerosols, each measuring a different part of the combustion continuum and overlapping each other in some cases. These methods can be basically divided into two groups: (i) chemical oxidation and (ii) thermal oxidation; some methods being a combination of the two and designated by the main oxidation reaction (Table 1).

The benzenepolycarboxylic acid marker method has been used to quantify charcoal BC in soils in Germany, the USA, Brazil and Russia (Glaser et al., 1998, 2000; Glaser & Amelung, 2003; Brodowski et al., 2005; Czimczik et al., 2003, 2005; Dai et al., 2005). Specific benzenepolycarboxylic acids, typical markers of pyrolysis reactions, are quantified and summed as BC after digestion in nitric acid at 170 °C.

[3] Graphene – a singular planar sheet of carbon atoms in 2-D (Stankovich et al., 2006)
[4] Aromaticity - a special stability resulting from a specific ring-structured planar molecule, with alternating single and double-bonded carbon atoms.

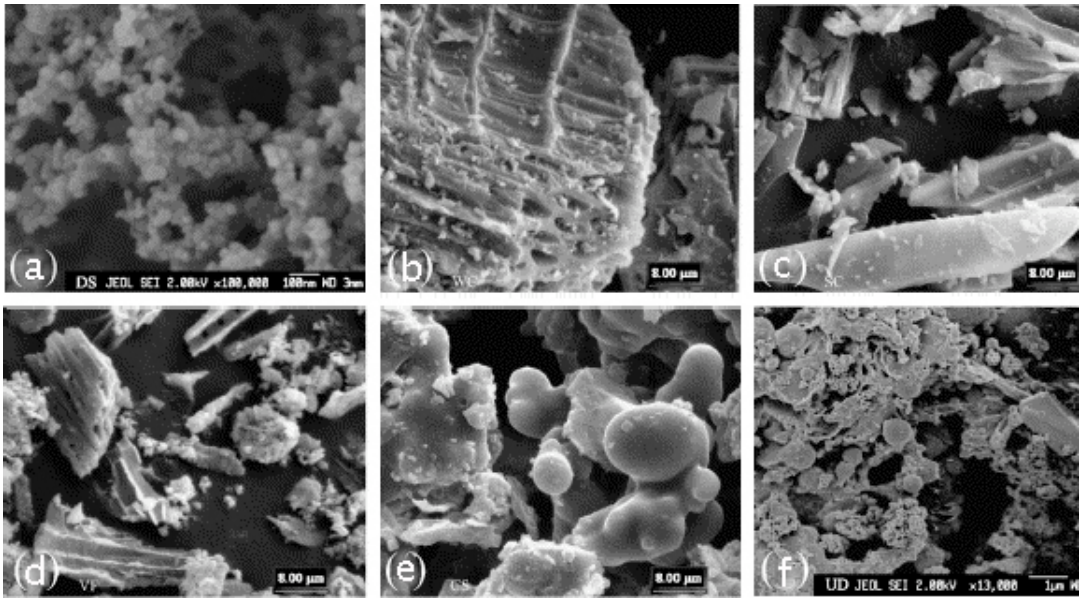

Fig. 4. Scanning electron micrographs of (a) diesel soot, (b) wood charcoal, (c) straw charcoal, (d) vegetation fire residues, (e) chimney soot and (f) urban dust (Fig. adapted from Fernandes et al., 2003)

The acid dichromate oxidation method has been mostly used to quantify BC in soils in southern Africa and Pacific deep-sea sediments (Wolbach & Anders, 1989; Lim & Cacher, 1996; Bird & Gröcke, 1997; Bird et al., 1999; Masiello & Druffel, 1998, 2002; Mitra et al., 2002; Song et al., 2002). The method measures all residual carbon left after acid treatment as black carbon. The UV-oxidation method has been used to measure BC in soils in Australia, Germany and the USA (Schmidt et al., 1999; Skjemstad et al., 1999, 2002; Ansley et al., 2006). This method also quantifies all residual carbon, but employs solid-state nuclear magnetic resonance (NMR[5]) spectroscopy to specifically quantify aromatic carbon. The sodium chlorite method has been mostly used to quantify BC in soils in Canada, the USA (Simpson and Hatcher, 2004). It is a harsh chemical method and most charcoal BC does not survive the oxidation. Thermogravimetry and differential scanning calorimetry have been used to quantify all carbonaceous species (including carbonates, oxalate) of organic matter, mostly in soils from France, Brazil and England (Dell' Abate et al., 2000, 2003; Plante et al., 2005; Lopez-Capel *et al*., 2005). The chemo-thermal oxidation method has been widely used to quantify soot-BC mainly in marine sediments off the coasts of the USA and Sweden (Gustafsson, et al., 2001; Gelinas et al., 2001; Elmquist et al., 2004). It employs a harsh oxidation at 375 °C and most charcoal BC does not survive the treatment (Elmquist et al., 2006). The thermal/optical transmittance or reflectance method is routinely used to quantify BC in aerosols and relies on collecting the sample on a filter paper *in situ* for stepwise thermal oxidation in a thermal analyzer (Chow et al., 1993, 2004; Birch and Cary, 1996; Huebert *et al*., 2004; Chen *et al*., 2005; Huang *et al*., 2006). There have been many intercomparative studies of this method and its variations (Schauer et al., 2003, Schmid et al., 2001), to standardize the method and ensure comparable data within atmospheric sciences.

Such a variety of methods, some chemical, some thermal, or a combination of the two, detect different ranges of the BC continuum, gives rise to incompatibility of quantification results across methods. In the first comparative exercise for BC quantification in soils, six different methods gave results that differed by two orders of magnitude (Schmidt et al., 2001). A lack of standard reference materials to analyse for BC, that are representative of most environments where BC is found, makes interlaboratory comparisons difficult. Additionly, some method parameters of the same method differ among laboratories, adding to the uncertainty of method comparisons.

[5] NMR - a phenomenon which occurs when the nuclei of certain atoms are subjected to a static magnetic field and exposed to a second oscillating magnetic field. The response of the nucleus in terms of its spin property gives insight into the chemistry and structure of the molecule.

Table 1. Summary of the most common BC quantification methods

Method name	Chemical oxidation	
BPCA	Benzene polycarboxylic acid (BPCA) formation (Brodowski et al., 2005)	Samples are oxidised in HNO_3 for 8 h after removal of polyvalent cations with acid, to form BPCAs from aromatic carbon. Quantification of formed BPCAs using a GC/FID.
Cr_2O_7	Acid dichromate oxidation (Wolbach & Anders, 1989)	Samples are oxidised in $K_2Cr_2O_7/H_2SO_4$ (varying timing) after acid pre-treatment. Quantification of the residual carbon as BC using elemental analysis.
UV	Ultraviolet (UV) photo-oxidation (Skjemstad et al., 1999)	Samples are photo-oxidised at 2.5 kW for 2 h in oxygen-saturated water. Quantification of the residual carbon as BC using ^{13}C NMR and elemental analysis.
NaClO	Sodium chlorite oxidation (Simpson & Hatcher, 2004)	Samples are oxidised three times with $NaClO_2$ for 4 h after acid pre-treatment. Quantification of the residual carbon as BC using ^{13}C NMR and elemental analysis.
	Thermal oxidation	
TG-DSC	Thermogravimetry and differential scanning calorimetry (DSC) (Lopez-Capel et al., 2005)	Samples are thermally oxidised at 300 °C and 450 °C and the mass loss recorded. The position of the DSC peaks reflects the structural and chemical composition of the material.
CTO-375	Chemo-thermal oxidation at 375 °C (Elmquist et al., 2004)	Samples are oxidised at 375 °C for 18 or 24 h after acid pretreatment. Quantification of the residual carbon as BC using elemental analysis.
TOT/TOR	Thermal optical transmittance or reflectance (Schmid et al., 2001)	Samples are heated stepwise to 900 °C under an oxygen/helium air mixture. Quantification of the residual carbon using laser transmittance or reflectance, followed by FID.

DEGRADATION AND STABILISATION OF BLACK CARBON

Most of the methods referenced above have been involved in the quantification of BC in relation to its decomposition and stability in natural environments. Such studies are very relevant since, although BC has long been thought to be relatively inert compared to plant residues, recent studies have shown that it can be degraded. Goldberg (1985) calculated, based on a conservative estimate of annual BC production from biomass burning of 0.1 Pg (1 Pg = 10^{15} g), that if BC did not break down, the earth's surface carbon would be turned into BC in <100 000 years; or like Druffel (2004) graphically asked "Why are we not knee-deep in charcoal?". Degradation of BC is thought to occur in soils through either chemical or biological oxidation, but results are inconsistent as to which process contributes the most to black carbon degradation. The first experiments to illustrate microbial breakdown were conducted in 1908, where the evolution of CO_2 and heat independently indicated microbial oxidation of charcoal (Potter, 1908). Laboratory incubation experiments conducted by Hamer et al. (2004) and Baldock & Smernik (2002), ranging from 60 to 120 days, at 20-25 °C, both indicated that microbial degradation of black carbon is dominant, by monitoring CO_2 evolution and percent organic carbon left after the incubation. Saprophytic fungi were also detected growing on 100-year old charcoal pieces found in a forest soil (Hockaday et al., 2006). On the other hand, Cheng et al. (2006) found that abiotic, chemical degradation was dominant in their incubation (120 days, 30-70 °C), where the authors observed a decrease in pH, and an increase in cation exchange capacity and oxygen content, only in the non-inoculated flasks. Cheng et al. (2006) concluded that further microbial degradation of black carbon could be facilitated by the initial abiotic oxidation. Apart from chemical or biological oxidation, Gouveia et al. (2002) mention that charcoal can also be pulverised by the swell and shrink actions of certain clays in soil horizons, although not much information is available regarding such physical degradation.

What does degraded black carbon look like? Recently, specialised spectroscopy using Scanning Transmission X-ray Microscopy (STXM) in conjunction with Near-Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy has shown that ancient charcoal (6000 BP), displayed a highly aromatic core, a progressively more oxidised region partly surrounding the core, and a non-continuous region surrounding the two former areas that showed higher carboxylic and phenolic signatures than aromatic and unsaturated signatures (Lehmann et al., 2005). Hockaday et al. (2006) also found condensed aromatic ring structures extensively substituted with oxygen-containing functional groups in the soil pore water of a forest site of intense biomass burning between 1890 and 1920, indicating degradation of charcoal black carbon on a centennial timescale.

Evidence of black carbon preservation is numerous, and indeed it is much more stable than other carbon forms, e.g. cellulose (Baldock & Smernik, 2002). Intact charcoal pieces, as well as other forms of BC have been found at depth in soils where in many cases the residence times exceed 1000 years (Glaser et al., 2001; Gouveia et al., 2002; Schmidt et al., 2002; Krull & Skjemstad, 2002). Stratified charcoal records from Europe, South-, Central- and North America, and Oceania give evidence of black carbon from ancient biomass burning, in some cases more than 7500 years old (Carcaillet et al., 2002). Not only charcoal pieces can be preserved; the aromatic ring structures found in the soil pore water mentioned above, being one example of charcoal transformed while its aromatic structure is not destroyed (Hockaday et al., 2006).

The enhanced recalcitrance of BC in soils may be linked not only to its refractory structure but also its protection by soil microaggregates and complexing with metal oxides (Krull et al., 2006). Brodowski et al. (2006) quantified the most black carbon in occluded particulate organic matter fractions compared to free particulate organic matter fractions, and also found selectively more black carbon compared to other organic carbon compounds in these occluded fractions. In some soils rich in iron and aluminium oxides, these oxides are strongly associated with the organic carbon and black carbon (Glaser et al., 1998; Wisemann & Püttmann, 2006). In a very detailed chemical oxidation study, Krull et al. (2006) concluded that protection by the mineral matrix might stabilise carbon in surface soils at decadal timescales, but that chemical recalcitrance controlled the longer-term stabilisation of the material.

Marine sediments are the ultimate sink for black carbon, and these black carbon deposits are also very long lived. Evidence of this has been found at various sites in the world's oceans (Masiello, 2004). Smith et al. (1973) extracted charcoal particles from deep-sea Pacific marine sediments that were many thousand years old. In two other deep-sea ocean sites in the northeastern Pacific, black carbon was found that is 2400 to 13900 carbon-14 years older than non-black sedimentary organic carbon deposited at the same time. This black carbon was probably aged on land and deposited in the deep ocean via aerosol or river transport (Masiello & Druffel, 1998).

The net effect of climate change at least in fire-prone regions of the world is not clear yet (not taking into account fossil fuel burning). It can either mean more fire, which in turn induces greater climate change, and creating a positive feedback loop that will make climate change control such as carbon sequestration more difficult. If climate change led to less fire, potential stabilisation of carbon could be conceivable (Lavorel et al., 2006). In the foreseeable future, increased research attention will focus on the stabilisation of black carbon, either natural or through anthropogenic means, such as slash-and-char, where 50% of the initial carbon is sequestered compared to only 3% retained after burning (Lehmann et al., 2006). More studies of BC turnover is also essential, e.g. how long it is stabilised in soil, since increased degradation of this potential carbon sink will remove one of the last candidates for sequestration of atmospheric carbon.

Objectives and outline of thesis

In an effort to answer questions regarding the impact of black carbon on global climate change and potential mitigation, quantification techniques should be as trustworthy as possible. To make sense of the disparate results from different quantification techniques, we proposed to establish a set of reference materials that can be used to (i) ensure long-term inter- and intra-laboratory data quality, and (ii) facilitate comparative analyses between different analytical techniques. The first objective here was to perform a **detailed chemical analysis of the reference materials.** From these results we extracted information on how the chemical and physical properties of the different black carbon reference materials may influence their detection by the various BC quantification methodologies (**Paper 1**).

Since charcoal reference materials did not exist, we synthesised two charcoals from different starting materials (wood and grass) for use as reference materials. The second objective was to analyse these synthesised charcoal and compare their characteristics to natural charcoals to see **how representative are laboratory-produced charcoal of natural charcoal (Paper 2)**.

To better compare results from different methods with these reference materials, we coordinated an international comparative exercise of different BC quantification methods. Objectives in this study were to (i) **quantify the variability of results for each method,** (ii) **discuss potential method biases,** and (iii) **identify the strengths and weaknesses of each method (Paper 3).**

From this comparative study, we concluded that the benzene polycarboxylic acid marker method, used in our laboratory gave reasonable results for soils and applied it in a study of black carbon turnover in order to contribute data for global black carbon budgets. The objectives were to (i) **calculate BC stocks** of a Chernozem soil on two dates, which have been sampled 100 years apart at the same location in the Russian steppe, and (ii) used the data to **estimate a turnover time of BC in this soil (Paper 4)**.

Thesis summary

"When you can measure what you are speaking about and express it in numbers you know something about it. But when you cannot measure it, when you cannot express it in numbers, your knowledge is of a meagre and unsatisfactory kind; it may be the beginning of knowledge, but you have scarcely, in your thoughts, advanced to the stage of *science*, whatever the matter may be."

Lord Kelvin, quoted from "The beak of the finch", Jonathan Weiner (1995)

ESTABLISHMENT OF BLACK CARBON REFERENCE MATERIALS

A standard set of reference materials for BC quantification in soils and sediments is invaluable in aiding to calibrate and explain trends of results from different methods. In order to do this, these reference materials should represent a wide range of environmental materials. Twelve materials were chosen for this purpose by the black carbon steering committee (Schmidt et al., 2003), primarily for an international ring trial to compare black carbon quantification methods in soils and sediments, but also to serve as reference materials for the environmental science community in calibrating and validating new or improved BC quantification methods. These materials are divided into three groups: (i) laboratory-produced BC-rich materials (n-hexane soot, wood char, grass char), (ii) non-BC materials that could potentially interfere with analysis (melanoidin, shale, bituminous coal, lignite coal), and (iii) environmental matrices that probably contain BC (urban aerosol, harbour marine sediment, two soils, dissolved organic matter). The materials were chosen to be easily available from suppliers, homogenous, inexpensive, and represent natural samples.

PRODUCTION OF CHARCOALS AS BLACK CARBON-RICH REFERENCE MATERIALS REPRESENTING NATURAL CHARCOALS

No char reference materials existed and they were specifically produced in this study to represent natural charcoal found in the environment after a burning event. Chestnut wood (*Castanea sativa*) was chosen to represent char from a forest fire. Ideally, more than one wood type should have been chosen, since they would behave differently during combustion, however, we believe that chestnut wood is representative enough of other wood species. The wood was obtained in a large enough quantity, from a known and detailed source to ensure the production of a long-term source of black carbon from wood. Grassland fires are the main other source of black carbon from biomass burning, occurring in many parts of the world, including sub-Saharan Africa, parts of North and South America, south-east Asia and Australia (Crutzen & Andreae, 1990; Kuhlbusch et al., 1996; Glaser & Amelung, 2003; Streets et al., 2003; Clark et al., 2005). Rice straw (*Oryza sativa*) was chosen to represent char from a grassland fire. Although grasses from around the world differ in morphology, the basic structure of grass is general enough for rice straw to be representative. The wood and grass straw were pyrolysed at 450 °C under a nitrogen atmosphere, which mimics the oxygen-free conditions on the inside of burning material at a moderate burning temperature.

In order to assess if these synthesised charcoals represent natural charcoals, the chars and their uncharred precursors were analysed for C, H, O, Fe and Al content, stable carbon-13 isotopes[6], specific surface area and aromaticity using NMR Cross Polarisation (CP) and Direct Polarisation (DP)[7], and compared to properties of natural chars where possible. Very little data exists in the literature where natural chars have been characterised for the abovementioned parameters and in most cases the formation temperature is not known. From the laboratory-produced chars described in the literature, we found a that an H/C atomic ratio > 0.5 correlated with a formation temperature < 500 °C, whereas chars with H/C < 0.5 were mostly formed at higher temperatures (500-1000 °C). Typical low temperature fires have temperatures between 400-500 °C. The H/C atomic ratios for the chars in this study, formed at 450 °C, were both above 0.5 (~0.7) (Fig. 5). Interestingly, the few naturals chars analysed for H/C, specific surface area and $\delta^{13}C$ value, display characteristics of high temperature burning. It could be that (1) natural fires do not form much char, due to the presence of oxygen and the preferential formation of ash, or (2) low temperature chars actually the chemically more resistant high-temperature chars.

[6] Stable carbon-13 isotopes: Atoms of the same atomic number but different atomic weights are called isotopes. Carbon has two stable isotopes, ^{12}C (98.89%) and ^{13}C (1.11%), which are used as a fractionation ratio to study changes in the environment, e.g. burning of material (Killops & Killops, 2005)

[7] CP: an NMR technique where magnetisation is transferred from the abundant ^{1}H population, which needs to be present, to the ^{13}C nuclei.

DP: an NMR technique where magnetisation is directly transferred to the ^{13}C nuclei, but takes longer than CP (Smernik & Oades, 2000).

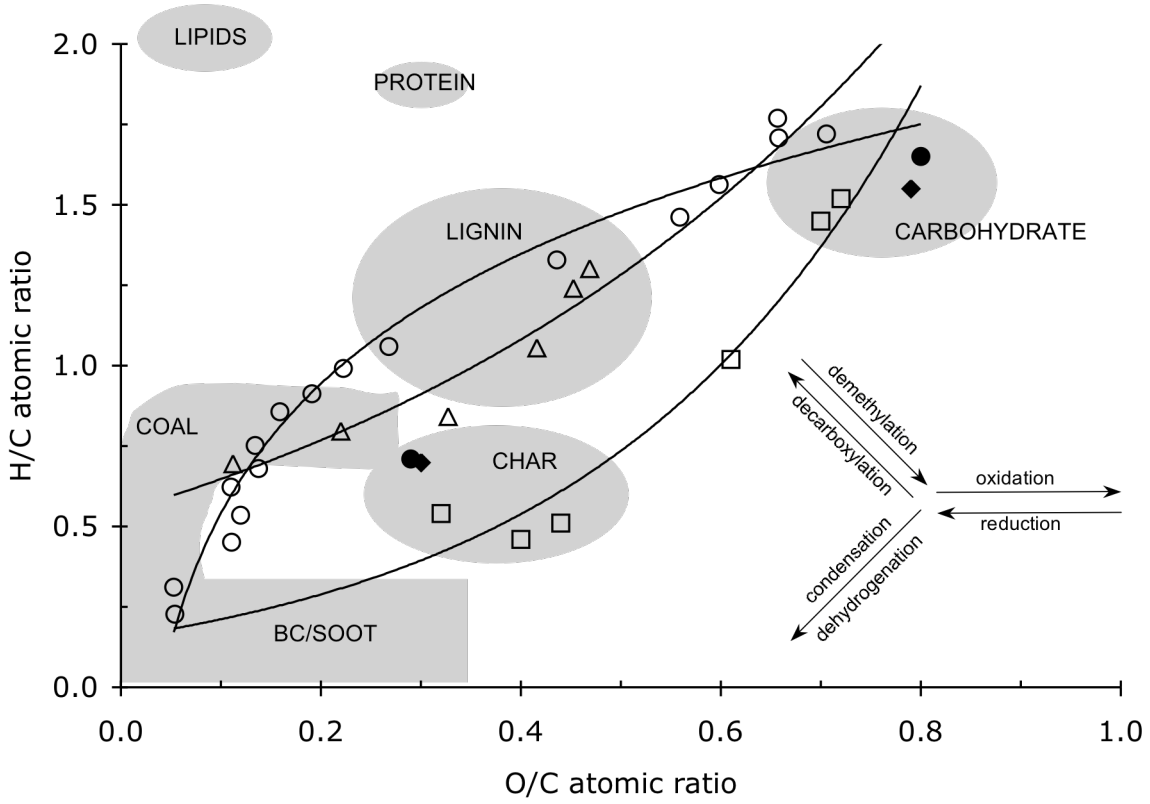

Fig. 5. Processes related to the charring of biomass – wood (filled diamonds) and grass straw (filled circles), before and after charring. Heating of other biomass materials: peas (open circles, (Braadbaart *et al.*, 2004), peat (open triangles, (Almendros *et al.*, 2003) and sapwood (open squares, (Baldock & Smernik, 2002). The grey shadings are areas of biomolecular components (adapted from Kim et al., 2003). (from **Paper 2**)

As have been found in other studies, the temperature of formation determines the degree of condensation of the char, e.g. how stable is it against degradation. This can be visualised in a plot of H/C and O/C atomic ratios of the materials. Plotted together with heated peas, peat, and sapwood from red pine, our chars behaved very much like any other biomass subjected to heating (Fig. 5).

Conclusively, taking these measured characteristics into account, we believe these char reference materials to be representative of natural chars that can be used in black carbon quantification studies.

COMPARISON OF BLACK CARBON QUANTIFICATION METHODS

The 12 black carbon reference materials introduced above were selected primarily for an international ring trial to compare black carbon quantification methods in soils and sediments. Black carbon was quantified in the reference materials by 17 international laboratories from different disciplines, using seven different methods (see Table 1 in Introduction), ranging from chemical to thermal oxidation or combinations thereof.

The results of the ring trial showed large variations in measured black carbon concentrations for all methods, even different laboratories using the same method. This is also visible in the plots of black carbon as percent of organic carbon, quantified by all the methods and averaged (Fig. 6). Disparate results are not new to such comparative studies, but since all laboratories used the same reference materials, we could make some conclusions about strengths and weaknesses of all the methods.

The ring trial produced a large data set (Fig. 6), which is discussed in more detail in Paper 3, but I will focus here on three materials from the different groups (environmental, black carbon-rich, non-black carbon) that summarise the results of this ring trial, indicated by the numbers 1-3 in circles in Fig. 6:

(1) The Vertisol is a sandy clay soil from Australia exposed to frequent fire events. There is no trend in the results from the different methods and values (BC as proportion of OC) range from 3.3-48.4%. Results for the other environmental matrices are equally disparate and dependent on the interactions of the heterogeneous material with different chemical and thermal oxidation agents.

(2) Most methods measured black carbon in the wood char (ranging from 24-100% BC/OC), except for two methods employing harsh thermal (oxidation at 375 °C) and chemical (sodium hypochlorite) oxidations respectively. These methods oxised all the char and had no residue to quantify. However, these methods quantified 50-70% BC/OC in the soot, and are thus the only two methods that could discern between the two different sources of black carbon – fossil fuels vs. biomass. These methods will underestimate black carbon concentrations in chars formed at lower temperatures that are not highly condensed like soot.

(3) All the methods but one quantified substantial amounts of black carbon in the bituminous coal (21-94% BC/OC), a material that contains no black carbon, while the CTO-375 method quantified only 2.3% BC/OC in this material. Most other non-black carbon interfering materials were also quantified to contain black carbon by most methods. These results should be viewed from the perspective that these materials (coal, shale) are usually present in insignificant amounts in most study areas, but should be noted when sampling takes place near a coal mine or exposed site. The melanoidin is the exception, where only the thermal/optical method measured almost 50% BC/OC in a material that contains no black carbon. The thermal/optical method is mostly used in atmospheric studies where the reflectance or transmittance of a material (related to its colour) is measured with heating to quantify black carbon on a sample collected on a filter *in situ* (in air).

In its current state, this method cannot be applied to soils and sediments, since any dark material irrespective of source is quantified as black carbon, while not necessarily having a combustion origin (see Introduction).

All the methods have advantages and disadvantages, and were designed to measure a certain window in the black carbon continuum. Therefore, there can be no "correct" value for black carbon. The results of this ring trial will also give insight to better understand already published data. This study has shown that method standardisation and refinement will be a continuing feature of black carbon quantification.

CHARACTERISATION OF THE BLACK CARBON REFERENCE MATERIALS

Could some of the disparate results of the ring trial be explained by the characteristics of the reference materials? The reference materials where chemically and physically analysed for C, H, O, Fe and Al content, colour, surface area and aromaticity – parameters that are important in a number of the BC quantification methodologies.

For example, the potassium dichromate (Cr_2O_7) method chemically oxidises all labile carbon, leaving a recalcitrant carbon residue that is quantified as BC. The hydrogen content of the materials is important for quantification methods employing nuclear magnetic (NMR) spectroscopy, like UV- and sodium hypochlorite oxidation. The proximity of hydrogen atoms to the carbon in question determines how well the aromatic carbon is quantified with magnetisation during cross polarisation. Thermal/optical methods determine BC using the reflectance or transmittance of the material, which is associated with the colour of the material. Metal oxides, like Fe and Al, play an important role in most quantification methods. These oxides can bind to aromatic carbon structures, inhibiting its detection. The surface area of the material determines to some extent its reaction potential with chemical and thermal agents.

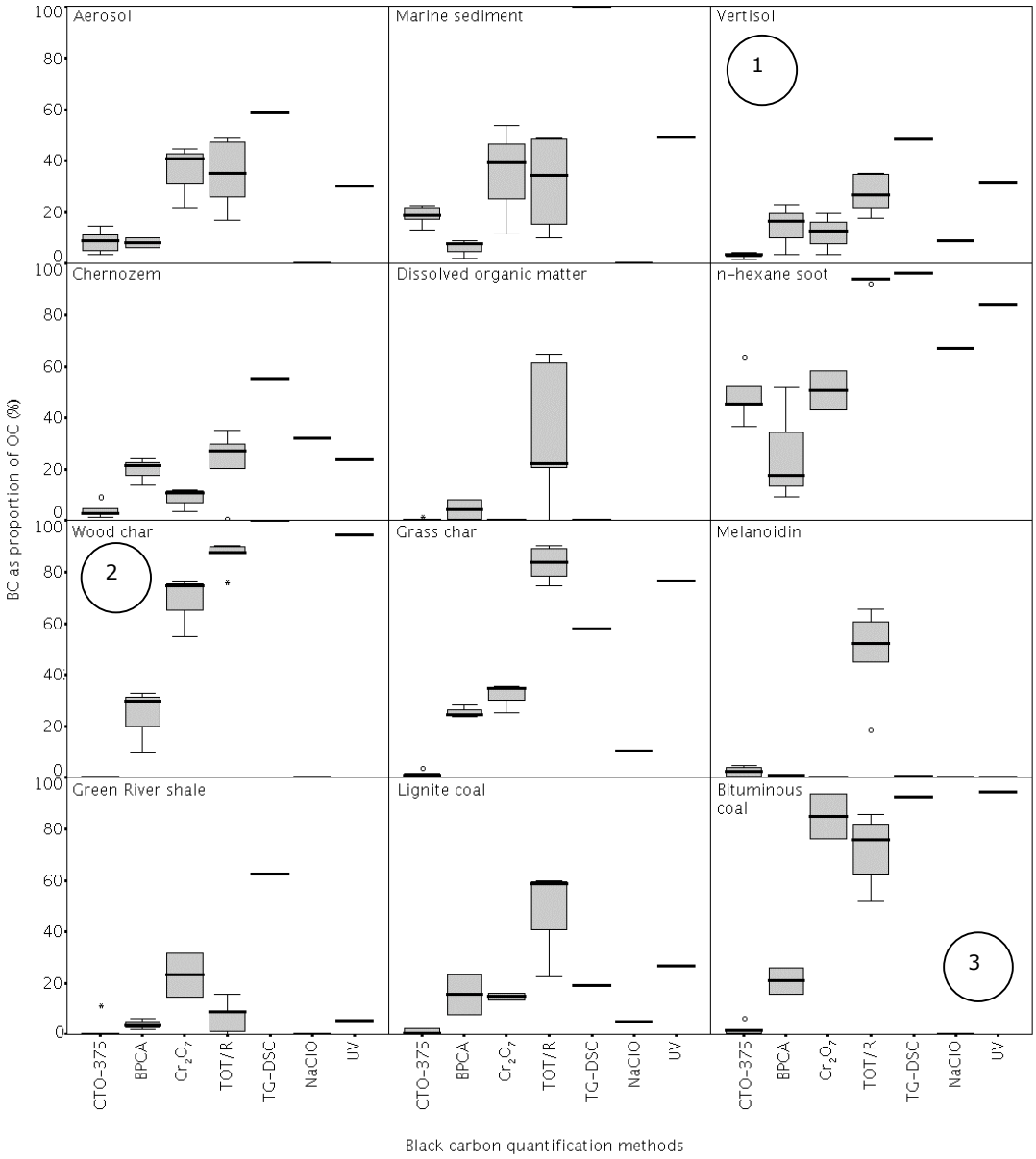

Fig. 6. Black carbon as proportion of organic carbon for each BC reference material quantified by seven different methods presented in boxplots showing median, percentiles (25%, 75%), minimum and maximum values. Outliers are represented by circles and extreme values by stars. For method CTO-375, N = 6; BPCA, N = 3; Cr_2O_7, N = 4; TOT/R, N = 5; TG-DSC, N = 1; NaClO, N = 1; UV, N = 1. See Table 1 for the method descriptions. (from **Paper 3**)

The BC-rich materials are mainly distinguished from one another in chemical structure, where the CP observability of the soot is much lower, and the surface area much higher than that of the chars. A low CP observability means that there are not enough H-atoms in the vicinity of the carbon in question to quantify it correctly. From Fig. 7 it can be seen that the soot has a very low H/C atomic ratio, meaning that not many H-atoms are available for sufficient magnetisation during cross polarisation, which could underestimate the amount of aromatic carbon in the material. The wood and grass chars have higher H/C ratios, are less condensed and thus more susceptible to chemical and thermal degradation.

Grass has the advantage that it contains a lot of silica in the form of phytoliths (silica capsules) that protect organic carbon and when charred, the black carbon, from degradation. The non-BC potentially interfering materials share properties with the BC-rich materials like high C-content, dark colour and high aromaticity, which are used for certain BC quantification methods. However, these materials do not have a pyrogenic origin, and these similarities can lead to false positive data and an overestimation of BC. It is important to differentiate between black carbon and non-black carbon materials in the environment, to quantify the specific contribution of biomass and fossil fuel combustion to the global carbon budget.

The environmental matrices have relatively high amounts of inorganic matter and metal oxides (mostly iron and aluminium) that increase their H/C and O/C atomic ratios (Fig. 7 and inset to Fig. 7). These metal oxides have the potential to catalyse or inhibit thermal and chemical reactions during BC analysis. Most BC quantification methods include a pre-treatment step to remove interfering compounds like iron and aluminium oxides. Thermal methods, like the thermal/optical and thermogravimetry techniques, do not remove metals before quantification. If present in large enough concentrations they could influence the reflectance or transmittance of a material by influencing the scatter of laser beams during thermal/optical quantification. Metals bound to black carbon can prevent it from being oxidised and measured during thermal analysis with the thermogravimetry method. These potential problems warrant further investigation.

These well-characterised reference materials supply a wealth of information on interactions of a variety of environmental materials with different quantification methods. Using these same materials for future methodological improvements and development of novel analytical approaches to quantify BC in environmental samples could prove to be invaluable in creating standard results that will be comparable, and is strongly recommended.

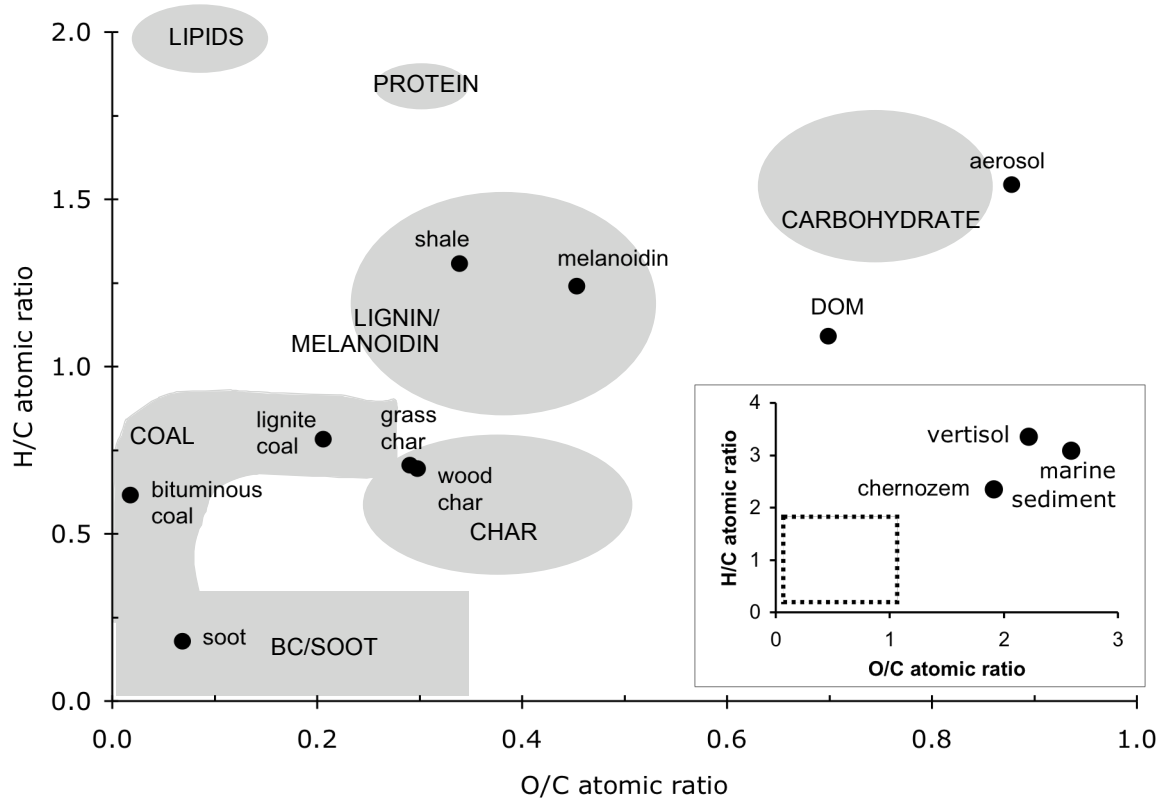

Fig. 7. Distinct groupings of individual biomolecular compounds (grey shading) for cellulose-rich material (carbohydrates), melanoidins, lignin (materials and monomers, charred materials (chars), different coals (coal) and soot. The groupings were adapted from Kim et al. (2003). The BC reference materials are plotted in relation to their H/C and O/C ratios and the grey shadings. The inset plot of Vertisol, Chernozem and marine sediment is on another scale than the rest of the reference materials. (from **Paper 1**)

APPLICATION OF A BLACK CARBON MARKER METHOD TO QUANTIFY BLACK CARBON TURNOVER IN A RUSSIAN STEPPE SOIL

A method that holds certain advantages over all the other quantification techniques is the benzene polycarboxylic acid (BPCA) marker method used in our laboratory (Table 1). Instead of only quantifying the bulk residual carbon after oxidation as BC, for example by elemental analysis, this method uses specific aromatic acids separated by gas chromatography/flame ionisation detection (GC/FID), to quantify black carbon. The BPCA method does not employ a harsh oxidation, so that both soot- and char-BC can be detected with it (Fig. 6). It is also subjected to artefact formation from other aromatic compounds like coal, and an assessment should be made to estimate how large the possible contamination from aromatic, non-BC materials can be. Otherwise, this method rather underestimates BC, since not all BC is converted to these acid markers. The method is briefly described in the appendix (Part C). We had the opportunity to apply this method in an interesting case study to determine black carbon turnover in a Russian steppe soil.

It has become evident that humans are changing the global carbon cycle (Janzen, 2004; IPCC, 2007). In order to quantify the change that has taken place and will take place in the future, we need to start measuring changes in black carbon too, in particular, stocks of BC in soils and sediments, since black carbon is a potential sequestration sink for carbon. Although BC is relatively inert in relation to plant residues for instance, it still degrades and could become part of the more rapidly cycling carbon again. This important fact has, however, only been tested in the laboratory and short-term field studies. There have been no assessments of black carbon turnover under long-term field conditions, and no estimation of soil black carbon stocks over the whole soil profile (lower than 20 cm). We took advantage of soils known to be sampled 100 years apart (1900, 1997, and 2004) from the same location in a Russian Chernozem preserve, along with known reduction in black carbon inputs after 1900, to quantify stocks and loss rates of black carbon *in situ* using the BPCA method introduced above.

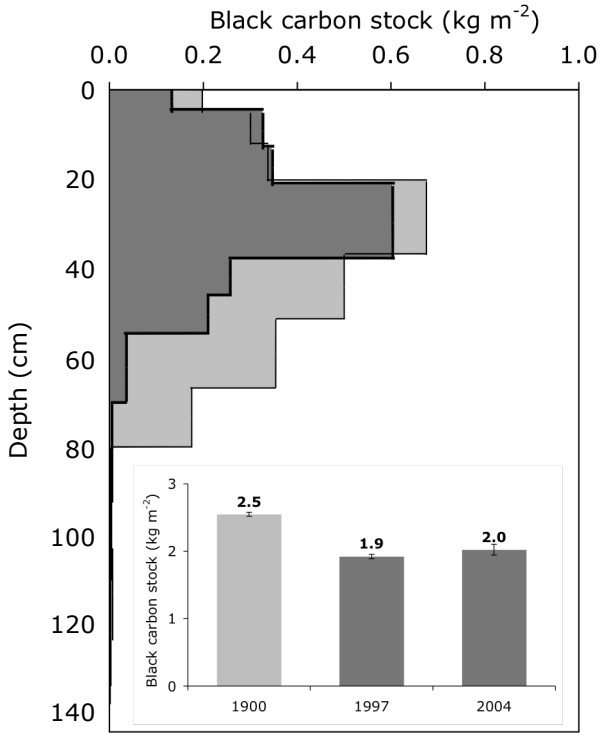

Fig. 8. Black carbon stocks of the 1900-soil (thin black line) and 1997-soil (thick black line), showing that there is less BC in the 1997-soil compared to the 1900-soil, with a suggested turnover time of between 212-541 years. Inset to Figure 1C shows that also total profile BC stocks decreased 25% between 1900 and 1997. The comparative 2004 soil is also about 25% lower. (from **Paper 4**)

The black carbon stock was degraded in the field over the 100 years, with a stock loss of 25% down to 130 cm depth (Fig. 8). Most other BC quantification studies report only the topsoil (up to 20 cm depth) values and thus potentially underestimate the BC stocks in these soils.

This two-point evaluation (1900 vs. 1997) allowed us to estimate the turnover time of the BC using the stock values of 1900 and 1997 in a simple model. We calculate the maximum turnover time of BC in this soil to be between 444 and 541 years, and the minimum being 212-262 years, with the ranges varying with assumptions about sampling interval, fire cessation, and bulk density. The implied turnover time of 212-541 years for black carbon in this soil is two to five times faster than the turnover time for inert carbon in the 2001 report by the Intergovernmental Panel on Climate Change. These results show that black carbon cannot be assumed to be a stable sink of carbon on century timescales. The paradigm is starting to shift from BC being inherently recalcitrant to mechanisms of occlusion and protection from degradation, for explaining the relative long turnover time and inert nature of black carbon.

Implications for black carbon research & future research perspectives

IMPLICATIONS FOR BLACK CARBON RESEARCH

From the **intercomparative study on black carbon quantification in soils and sediments** described in this thesis, it has become clear that methodological refinement and standardisation will still be needed in the foreseeable future. Laboratories that use the same method should ask among themselves: “Why do some laboratories use 900 °C for thermal oxidation and others 870 °C?” or “Why do some use a 24 hour digestion time and others only 18 hours” or “Why do some use a particular standard while others use another?” Standardising quantification methods will go a long way in ensuring comparable results.

A set of **standard black carbon reference materials** has been established, that can serve the black carbon community in calibrating and validating results of black carbon studies. This will aid in a better understanding of black carbon in relation to processes and reactions that it partakes in, in the laboratory and field.

Representative black carbon-rich materials have been produced for future black carbon research. The production technique ensures that this source of black carbon-rich materials, which is representative of natural black carbon, can be consistently produced in future.

The **benzene polycarboxylic acid marker method** used to study the turnover time of black carbon in a soil, produced reliable results and can be recommended to quantify black carbon in soils.

Chernozems are among the most black carbon-rich soils globally. We calculated that the **turnover time of black carbon** in this soil was two to five times faster than previously believed. This places a big question mark over the potential for soils to sequester atmospheric carbon, since black carbon is not as inert as the current paradigm suggests.

PERSPECTIVES FOR FUTURE BLACK CARBON RESEARCH

Chemical characterisation of natural charcoals

The formation conditions (temperature, atmosphere) of char from biomass burning define its chemical structure to a large extent, and how it will behave during degradation or analysis. However, very little chemical information on natural chars exist, as we discovered in Paper 1, where we compared our synthesised chars to natural chars. Setting up a database of the chemical properties, e.g. H/C and O/C atomic ratios, of natural chars from different starting materials (wood, grass), could be invaluable in testing the hypothesis that these ratios give an indication of the fire temperature during formation. This information could be important for BC method calibration, since some oxidation methods are harsher than others, depending on the formation conditions and type of char. Another interesting application would be to use this tool in archaeological studies to determine the temperature of prehistoric fires, discerning for example between land clearing fires and cooking fires, where the latter probably used higher temperatures than the former.

Improved set of black carbon reference materials

The current set of reference materials, although suitable for the task of calibrating black carbon quantification techniques, includes only a limited variety of environmental scenarios. It would be useful to include a few other reference materials that could broaden the scope of the current set.

Possible candidates include:

- **Diesel soot** – this would represent an environmentally relevant soot produced from engine exhaust. Such a diesel soot is available from the National Institute of Standards and Technology (NIST), as standard reference material (SRM) 1650b. However, this reference material costs $522 for 200 mg, and it would probably be more widely used if another less expensive source can be found. Currently, fossil fuel combustion condensates are represented by n-hexane soot, artificially produced from a hexane flame in the laboratory.
- **High temperature char** – a wood char produced at a temperature above 500 °C would represent a more condensed material that will be more resistant to degradation. This material can be produced at the EMPA Material Science and Technology, as described in Paper 1, by using the same starting material (chestnut wood) as the char reference material. Currently, two chars (wood and grass) produced at 450 °C represent low temperature biomass from two sources.
- **River sediment** – rivers are known to transport black carbon to the ocean, but very little data exists on the quantities exported. A typical river sediment, known to contain black carbon, would help to calibrate methods in measuring black carbon from such environments. Dissolved organic matter from the Suwannee river (issued by the International Humic Substance Society) is currently the representative of dissolved black carbon from river water. However, this material probably contains too little black carbon in dissolved format or methods are not calibrated yet to quantify black carbon in dissolved form.
- **Open ocean marine sediment** – the ultimate sink for black carbon does not have a reference material yet. Marine sediments are currently represented by a harbour sediment heavily polluted with soot from fossil fuel combustion. This material is also acquired from NIST and thus relatively expensive.

A follow-up intercomparative study on black carbon quantification methods

This first multi-method, multi-lab, multi-sample comparative study was a step in the right direction of ensuring more comparable results among methods. However, there are more steps like that needed before we can be satisfied that black carbon is quantified accurately enough. Therefore, a follow-up ring trial is necessary to address problems that became evident from the first ring trial.

Three problems that need to be addressed are:

1. **Number of reference materials analysed** by one laboratory – in order to get as much data as possible to compare, each laboratory needs to analyse all the reference materials that are part of the study.
2. **Method parameters** among laboratories using the same method – results from different laboratories using the same method will be easier to compare when all method parameters are equal. Laboratories using the same method should use for example, the same digestion time, temperature and acid concentrations.
3. **Number of laboratories using a method** – for statistical analysis and better comparability of results, more than one laboratory need to use a method in such a comparative study. This will give better insight into method problems and how results among different laboratories compare.

References

Akhter, M.S., Chughtai, A.R., Smith, D.M. (1985) The structure of hexane soot I: Spectroscopic studies. Applied Spectroscopy 39(1), 143-153.

Almendros, G., Knicker, H., Gonzalez-Vila, F.J. (2003) Rearrangement of carbon and nitrogen forms in peat after progressive thermal oxidation as determined by solid-state ^{13}C- and ^{15}N-NMR spectroscopy. Organic Geochemistry 34, 1559-1568.

Andreae, M.O., Gelenscér, A. (2006) Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols. Atmospheric Chemistry and Physics 6, 3131-3148.

Ansley, R.J., Boutton, T.W., Skjemstad, J.O. (2006) Soil organic carbon and black carbon storage and dynamics under different fire regimes in temperate mixed-grass savanna. Global Biogeochemical Cycles 20, GB3006, doi:10.1029/2005GB002670.

Baldock, J.A., Smernik, R.J. (2002) Chemical composition and bioavailability of thermally altered Pinus resinosa (Red pine) wood. Organic Geochemistry 33, 1093-1109.

Birch, M.E., Cary, R.A. (1996) Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. Aerosol Science & Technology 25(3), 221-241.

Bird, M.I., Gröcke, D.R. (1997) Determination of the abundance and carbon isotope composition of elemental carbon in sediments. Geochimica et Cosmochimica Acta 61(16), 3413-3423.

Bird, M.I., Moyo, C., Veenendal, E.M., Lloyd, J., Frost, P. (1999) Stability of elemental carbon in a savanna soil. Global Biogeochemical Cycles 13(4), 923-932.

Braadbaart, F., Boon, J.J., Veld, H., David, P., Van Bergen, P.F. (2004) Laboratory simulations of the transformation of peas as a result of heat treatment: changes of the physical and chemical properties. Journal of Archaeological Science 31, 821-833.

Brodowski, S., Rodionov, A., Haumeier, L., Glaser, B., Amelung, W. (2005) Revised black carbon assesment using benzene polycarboxylic acids. Organic Geochemistry 36, 1299-1310.

Brodowski, S., John, B., Flessa, H., Amelung, W. (2006) Aggregate-occluded black carbon in soil. European Journal of Soil Science 57, 539-546.

Carcaillet, C., Almquist, H., Asnong, H., Bradshaw, R.H.W., Carrión, J.S., Gaillard, M.-J., Gajewski, K., Haas, J.N., Haberle, S.G., Hadorn, P., Müller, S.D., Richard, P.J.H., Richoz, I., Rösch, M., Sánchez Goñi, M.F., von Stedingk, H., Stevenson, A.C., Talon, B., Tardy, C., Tinner, W., Tryterud, E., Wick, L., Willis, K.J. (2002) Holocene biomass burning and global dynamics of the carbon cycle. Chemosphere 49, 845-863.

Chen, Y., Sheng, G., Bi, X., Feng, Y., Mai, B., Fu, J. (2005) Emission factors for carbonaceous particles and polycyclic aromatic hydrocarbons from residential coal combustion in China. Environmental Science & Technology 39, 1861-1867.

Cheng, C.-H., Lehmann, J., Thies, J.E., Burton, S.D., Engelhard, M.H. (2006) Oxidation of black carbon by biotic and abiotic processes. Organic Geochemistry 37 (11): 1477-1488.

Chow, J.C., Watson, J.G., Pritchett, L.C., Pierson, W.R., Frazier, C.A., Purcell, R.G. (1993) The DRI Thermal/Optical Reflectance carbon analysis system: Description, evaluation and applications in U.S. air quality studies. Atmospheric Environment 27A (8), 1185-1201.

Chow, J.C., Watson, J.G., Chen, L.-W.A., Arnott, W.P., Moosmüller. H. (2004) Equivalence of elemental carbon by thermal/optical reflectance and transmittance with different temperature protocols. Environmental Science & Technology 38, 4414-4422.

Clark, T.L., Reeder, M.J., Griffiths, M., Packham, D., Krusel, N. (2005) Infrared observations and numerical modelling of grassland fires in the Northern Territory, Australia. Meteorology and Atmospheric Physics 88, 193-201.

Crutzen, P.J., Andreae, M.O. (1990) Biomass burning in the tropics: impact on atmospheric chemistry and biogeochemical cycles. Science 250, 1669-1678.

Czimczik, C.I., Preston, C.M., Schmidt, M.W.I. & Schulze, E.-D. (2003) How surface fire in Siberian Scots pine forests affects soil organic carbon in the forest floor: stocks, molecular structure, and conversion to black carbon (charcoal). Global Biogeochemical Cycles 17(1), 1020, doi:10.1029/2002/GB001956.

Czimczik, C.I., Schmidt, M.W.I., Schulze, E.-D. (2005) Effects of increasing fire frequency on black carbon and organic matter in Podzols of Siberian Scots pine forests. European Journal of Soil Science 56, 417-428.

Dai, X., Boutton, T.W., Glaser, B., Ansley, R.J., Zech, W. (2005) Black carbon in a temperate mixed-grass savanna. Soil Biology & Biochemistry 37, 1879-1881.

Dell' Abate, M.T., Canali, S., Trinchera, A., Benedetti, A., Sequi, P. (2000) Thermal method of organic matter maturation monitoring during composting process. Journal of Thermal and Analytical Calorimetry 61, 389-396.

Dell' Abate, M.T., Benedetti, A., Brookes, P.C. (2003) Hyphenated techniques of thermal analysis for characterisation of soil humic substances. Journal of Separation Sciences 26, 433-440.

Druffel, E.R.M. (2004) Comments on the importance of black carbon in the global carbon cycle. Marine Chemistry 92, 197-200.

Eckmeier, E., Rösch, M., Erhmann, O., Schmidt, M.W.I., Schier, W., Gerlach, R. Conversion of biomass to charcoal and the carbon mass balance from experimental slash-and-burn in a temperate deciduous forest. The Holocene, in press.

Elmquist, M., Gustafsson, Ö., Andersson, P. (2004) Quantification of sedimentary black carbon using the chemothermal oxidation method: an evaluation of ex situ pretreatments and standard additions approach. Limnology and Oceanography 2, 417-427.

Elmquist, M., Cornelissen, G., Kukulska, Z., Gustafsson, Ö. (2006) Distinct oxidative stabilities of char versus soot black carbon: Implications for quantification and environmental recalcitrance. Global Biogeochemical Cycles 20, GB2009, doi:10.1029/2005GB002629.

Etheridge, D.M., Steele, L.P., Langenfelds, R.L., Francey, R.J., Barnola, J.-M., Morgan, V.L. (1996) Natural and anthropogenic changes in atmospheric CO2 over the last 1000 years from air in Antarctic ice and firn. Journal of Geophysical Research – Atmosphere 101(D2), 4115-4128.

Fernandes, M.B., Skjemstad, J.O., Johnson, B.B., Wells, J.D., Brooks, P. (2003) Characterization of carbonaceous combustion residues. I. Morphological, elemental and spectroscopic features. Chemosphere 51, 785-795.

Forbes, M.S., Raison, R.J., Skjemstad, J.O. (2006) Formation, transformation and transport of black carbon (charcoal) in terrestrial and aquatic ecosystems. Science of the Total Environment 370, 190-206.

Fraser, M.P., Lakshmanan, K. (2000) Using levoglucosan as a molecular marker for the long-range transport of biomass combustion aerosols. Environmental Science & Technology 34, 4560-4564.

Gélinas, Y., Prentice, K.M., Baldock, J.A., Hedges, J.I. (2001) An improved thermal oxidation method for the quantification of soot/graphitic black carbon in sediments and soils. Environmental Science & Technology 35(17), 3519-3525.

Glaser, B., Amelung, W. (2003) Pyrogenic carbon in native grassland soils along a climosequence in North America. Global Biogeochemical Cycles 17(2), 1064, doi: 10.1029/2002GB002019.

Glaser, B., Haumaier, L., Guggenberger, G., Zech, W. (1998) Black carbon in soils: the use of benzenecarboxylic acids as specific markers. Organic Geochemistry 29(4), 811-819.

Glaser, B., Balashov, E., Haumaier, L., Guggenberger, G., Zech, W. (2000) Black carbon in density fractions of anthropogenic soils of the Brazilian Amazon region. Organic Geochemistry 31, 669-678.

Glaser, B., Haumaier, L., Guggenberger, G., Zech, W. (2001) The "Terra Preta" phenomenon: a model for sustainable agriculture in the humid tropics. Naturwissenschaften 88, 37-41.

Glaser, B., Lehmann, J., Zech, W. (2002) Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal – a review. Biology and Fertility of Soils 35, 219-230.

Glaser, B., Dreyer, A., Bock, M., Fiedler, S., Mehring, M., Heitmann, T. (2005) Source apportionment of organic pollutants of a highway-traffic-influenced urban area in Bayreuth (Germany) using biomarker and stable carbon isotope signatures. Environmental Science & Technology 39(11), 3911-3917.

Goldberg, E.D. (1985) Black carbon in the environment, 198 pp., John Wiley & Sons, Inc., New York.

Gouveia, S.E.M., Pessenda, L.C.R., Aravena, R., Boulet, R., Scheel-Ybert, R., Bendassoli, J.A., Ribeiro, A.S., Freitas, H.A. (2002) Carbon isotopes in charcoal and soils in studies of paleovegetation and climate changes during the late Pleistocene and the Holocene in the southeast and certerwest regions of Brazil. Global and Planetary Changes 33, 95-106.

Gustafsson, Ö., Haghseta, F., Chan, C., Macfarlane, J., Gschwend, P.M. (1997) Quantification of the dilute sedimentary soot phase: Implications for PAH speciation and bioavailability. Environmental Science & Technology 31, 203-209.

Gustafsson, Ö., Bucheli, T.D., Kukulska, Z., Andersson, M., Largeau, C., Rouzaud, J.-N., Reddy, C.M., Eglinton, T.I. (2001) Evaluation of a protocol for the quantification of black carbon in sediments. Global Biogeochemical Cycles 15(4), 881-890.

Hamer, U., Marschner, B., Brodowski, S., Amelung, W. (2004) Interactive priming of black carbon and glucose mineralization. Organic Geochemistry 35, 823-830.

Hockaday, W.C.H., Grannas, A.M., Kim, S., Hatcher, P.G. (2006) Direct molecular evidence for the degradation and mobility of black carbon in soils from ultrahigh-resolution mass spectral analysis of dissolved organic matter from a fire-impacted forest soil. Organic Geochemistry 37, 501-510.

Huang, L., Brook, J.R., Zhang, W., Li, S.M., Graham, L. Ernst, D. Chiculescu, A., Lu, G. (2006) Stable isotope measurements of carbon fractions (OC/EC) in airborne particulate: A new dimension for source characterization and apportionment. Atmospheric Environment 40(15), 2690-2705.

Huebert, B.J., Bertram, T., Kline, J., Howell, S.G., Eatough, D., Blomquist, B. (2004) Measurements of organic and elemental carbon in Asian outflow during ACE-Asia from the NSF/NCAR C-130. Journal of Geophysical Research 109, D19S11, doi:10.1029/2004JD004700.

Intergovernmental Panel on Climate Change (IPCC), Climate Change 2001: The Scientific Basis. J.T. Houghton et al., Eds. (Cambridge Univ. Press, New York, 2001).

Intergovernmental Panel on Climate Change (IPCC), Climate Change 2007: The physical science basis. Summary for policy makers. Contribution of Working Group I to the assessment report of the Intergovernmental Panel on Climate Change.

Janzen, H.H. (2004) Carbon cycling in earth systems – a soil science perspective. Agriculture, Ecosystems and Environment 104, 399-417.

Jonker, M.T.O., Koelmans, A.A. (2002) Sorption of polycyclic aromatic hydrocarbons and polychlorinated biphenyls to soot and soot-like materials in the aqueous environment mechanistic considerations. Environmental Science and Technology 36, 3725-3734.

Killops, S.D., Killops, V.J. (2005) An Introduction to Organic Geochemistry. Blackwell Science Ltd.

Kim, S., Kramer, R.W., Hatcher, P.G. (2003) Graphical method for analysis of ultrahigh-resolution broadband mass spectra of natural organic matter, the Van Krevelen diagram. Analytical Chemistry 75, 5336 - 5344.

Koelmans, A.A., Jonker, M.T.O., Cornelissen, G., Bucheli, T.D., Van Noort, P.C.M., Gustafsson, Ö. (2006) Black carbon: The reverse of its dark side. Chemosphere 63, 365-377.

Krull, E.S., Skjemstad, J.O. (2002) $\delta^{13}C$ and $\delta^{15}N$ profiles in 14C-dated Oxisol and Vertisols as a function of soil chemistry and mineralogy. Geoderma 1890, 1-29.

Krull, E.S., Swanston, C.W., Skjemstad, J.O., McGowan, J.A. (2006) Importance of charcoal in determining the age and chemistry of organic carbon in surface soils. Journal of Geophysical Research 111, G04001, doi: 10.1029/2006JG000194.

Kuhlbusch, T.A.J. (1995) Method for determining black carbon in residues of vegetation fires. Environmental Science & Technology 29, 2695-2702.

Kuhlbusch, T.A.J., Crutzen, P.J. (1995) Toward a global estimate of black carbon in residues of vegetation fires representing a sink of atmospheric CO_2 and a source of O_2. Global Biogeochemical Cycles 9(4), 491-501.

Kuhlbusch, T.A.J., Andreae, M.O., Cachier, H., Goldammer, J.G., Lacaux, J.-P., Shea, R., Crutzen, P.J. (1996) Black carbon formation by savanna fires: Measurements and implications for the global carbon cycle. Journal of Geophysical Research 101(D19), 23, 651-23,666.

Lavorel, S., Flannigan, M.D., Lambin, E.F., Scholes, M.C. (2006) Vulnerability of land systems to fire: Interactions among humans, climate, the atmosphere, and ecosystems. Mitigation and Adaption Strategies for Global Change 12, 33-53.

Lehmann, J., Liang, B., Solomon, D., Lerotic, M., Luizão, F., Kinyangi, J., Schäfer, T., Wirick, S. Jacobsen, C. (2005) Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy for mapping nano-scale distribution of organic carbon forms in soil: Application to black carbon particles. Global Biogeochemical Cycles 19, GB1013, doi:10.1029/2004GB002435.

Lehmann, J., Gaunt, J., Rondon, M. (2006) Bio-char sequestration in terrestrial ecosystems – a review. Mitigation and Adaption Strategies for Global Change 11, 403-427.

Lim. B., Cachier, H. (1996) Determination of black carbon by chemical oxidation and thermal treatment in recent marine and lake sediments and Cretaceous-Tertiary clays. Chemical Geology 131, 143-154.

Lopez-Capel, E., Sohi, S.P., Gaunt, J.L., Manning, D.A.C. (2005) Use of thermogravimetry-differential scanning calorimetry to characterize modelable soil organic matter fractions. Soil Science Society of America Journal 69(1), 136-140.

Masiello, C.A. (2004) New directions in black carbon organic geochemistry. Marine Chemistry 92, 201-213.

Masiello, C.A., Druffel, E.R.M. (1998) Black carbon in deep-sea sediments. Science 280, 1911-1913.

Masiello, C.A., Druffel, E.R.M., Currie, L.A. (2002) Radiocarbon measurements of black carbon in aerosols and ocean sediments. Geochimica et Cosmochimica Acta 66(6), 1025-1036.

Mitra, S., Bianchi, T.S., McKee, B.A., Sutula, M. (2002) Black carbon from the Mississippi River: quantities, sources and potential implications for the global carbon cycle. Environmental Science & Technology 36, 2296-2302.

Novakov, T. (1984) The role of soot and primary oxidants in atmospheric chemistry. Science of the Total Environment 36, 1-10.

Plante, A.F., Pernes, M., Chenu, C. (2005) Changes in clay-associated organic matter quality in a C depletion sequence as measured by differential thermal analyses. Geoderma 129(3-4), 186-199.

Potter, M.C. (1908) Bacteria as agents in the oxidation of amorphous carbon. Proceedings of the Royal Society of London, Series B 80(539), 239-259.

Preston, C.M., Schmidt, M.W.I. (2006) Black (pyrogenic) carbon: a synthesis of current knowledge and uncertainties with special consideration of boreal regions. Biogeoscience 3, 397-420.

Rumpel, C., Chaplot, V., Planchon, O., Bernadou, J., Valentin, C., Mariotti, A. (2006) Preferential erosion of black carbon on steep slopes with slash and burn agriculture. Catena 65, 30-40.

Schauer, J.J., Mader, B.T., Deminter, J.T., Heidemann, G., Bae, M.S., Seinfeld, J.H., Flagan, R.C., Cary, R.A., Smith, D., Huebert, B.J., Bertram, T., Howell, S., Kline, J.T., Quinn, P., Bates, T., Turpin, B., Lim, H.J., Yu, J.Z., Yang, H., Keywood, M.D. (2003) ACE-Asia intercomparison of a thermal-optical method for the determination of particle-phase organic and elemental carbon. Environmental Science & Technology 37, 993-1001.

Schmid, H., Laskus, L., Abraham, H.J., Baltensberger, U., Lavanchy, V., Bizjak, M., Burba, P., Cachier, H., Crow, D., Chow, J., Gnauk, T., Even, A., Ten Brink, H.M., Giesen, K.-P., Hitzenberger, R., Hueglin, C., Maenhaut, W., Pio, C., Carvalho, A., Putaud, J.-P., Toom-Sauntry, D., Puxbaum, H. (2001) Results of the "carbon conference" international aerosol carbon round robin test stage I. Atmospheric Environment 35, 2111-2121.

Schmidt, M.W.I., Skjemstad, J.O., Gehrt, E., Kögel-Knabner, I. (1999) Charred organic carbon in German chernozemic soils. European Journal of Soil Science 50, 351-365.

Schmidt, M.W.I., Noack, A.G. (2000) Black carbon in soils and sediments: Analysis, distribution, implications, and current challenges. Global Biogeochemical Cycles 14, 777-794.

Schmidt, M.W.I., Skjemstad, J.O., Czimczik, C.I., Glaser, B., Prentice, K.M., Gelinas, Y., Kuhlbusch, T.A.J. (2001) Comparative analysis of black carbon in soils. Global Biogeochemical Cycles 15(1), 163-167.

Schmidt, M.W.I., Skjemstad, J.O., Jäger, C. (2002) Carbon isotope geochemistry and nanomorphology of soil black carbon: Black chernozemic soils in central Europe originate from ancient biomass burning. Global Biogeochemical Cycles 16(4), 1123, doi:10.1029/2002GB001939.

Schmidt, M.W.I., Masiello, C.A., Skjemstad, J.O. (2003) Final recommendations for reference materials in black carbon analysis. EOS Transactions AGU 84(52), 582-583.

Simpson, M.J., Hatcher, P.G. (2004) Determination of black carbon in natural organic matter by chemical oxidation and solid-state 13C nuclear magnetic resonance spectroscopy. Organic Geochemistry 356, 923-935.

Skjemstad, J.O., Taylor, J.A., Smernik, R.J. (1999) Estimation of charcoal (char) in soils. Communications in Soil Science and Plant Analysis 30, 2283-2298.

Skjemstad, J.O., Reicosky, D.C., Wilts, A.R., McGowan, J.A. (2002) Charcoal carbon in U.S. agricultural soils. Soil Science Society of America Journal 66, 1249-1255.

Smernik, R.J., Oades, J.M. (2000) The use of spin counting for determining quantitation in solid state ^{13}C NMR spectra of natural organic matter. 1. Model systems and the effects of paramagnetic impurities. Geoderma 96, 101-129.

Smith, D.J., Griffen, J.J., Goldberg, E.D. (1973) Elemental carbon in marine sediments: a baseline for burning. Nature 241, 268-270.

Song, J., Peng, P., Huang, W. (2002) Black carbon and kerogen in soils and sediments. 1. Quantification and characterization. Environmental Science & Technology 36, 3960-3967.

Stankovich, S., Dikin, D.A., Dommett, G.H.B., Kohlhaas, K.M., Zimney, E.J., Stach, E.A., Piner, R.D., Nguyen, S.T., Ruoff, R.S. (2006) Graphene-based composite materials. Nature 442, 282-286.

Streets, D.G., Yarber, K.F., Woo, J.-H., Carmichael, G.R. (2003) Biomass burning in Asia: Annual and seasonal estimates and atmospheric emissions. Global Biogeochemical Cycles 17(4), 1099, doi:10.1029/2003GB002040.

Watson, A.Y., Valberg, P.A. (2001) Carbon black and soot: two different substances. American Industrial Hygiene Association Journal (AIHAJ) 62, 218-228.

Wiseman, C.L.S., Püttmann, W. (2006) Interactions between mineral phases in the preservation of soil organic carbon. Geoderma 134, 109-118.

Wolbach, W.S., Anders, E. (1989) Elemental carbon in sediments: determination and isotopic analysis in the presence of kerogen. Geochimica et Cosmochimica Acta 53, 1637-1647.

Appendix

BLACK CARBON QUANTIFICATION METHOD: BENZENE POLYCARBOXYLIC ACIDS AS MARKERS

This method was used to quantify black carbon in the Russian steppe soils analysed in Paper 3 and Paper 4.

Benzene polycarboxylic acids

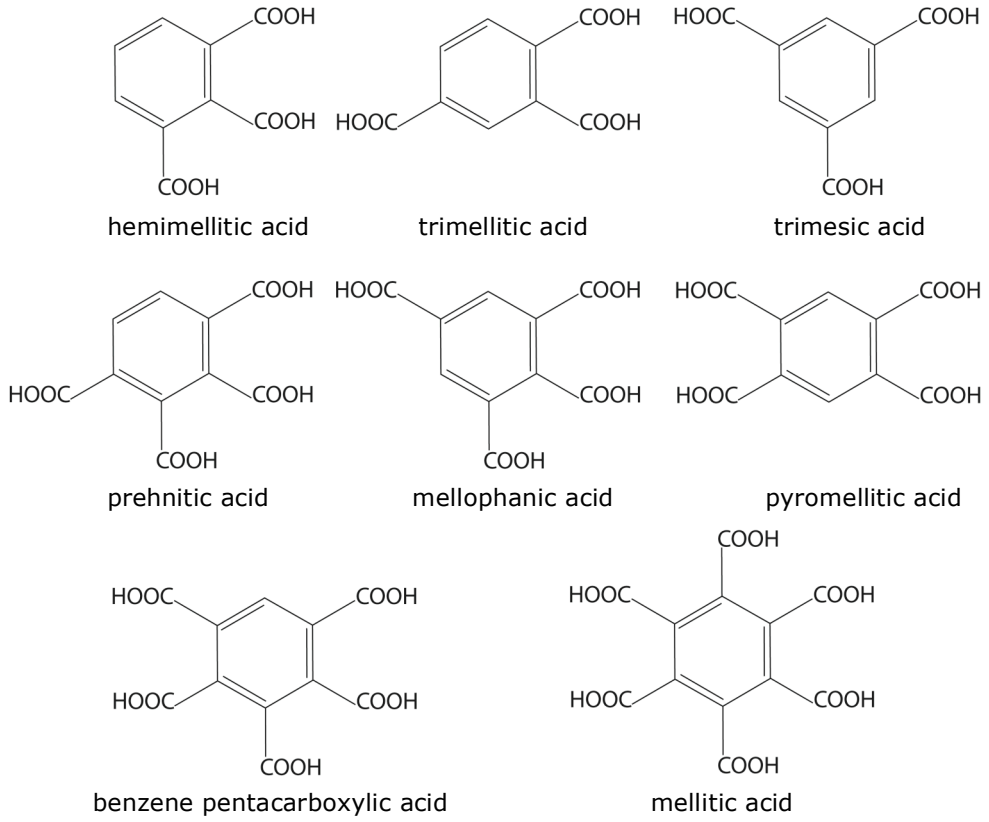

Fig. 1. Structures of benzene polycarboxylic acids (BPCAs) used as markers for black carbon assessment (from Brodowski et al., 2005). All these acids are available as standards, used in a standard series, except prehnitic and mellophanic acid.

Analytical procedure

Elimination of polyvalent cations, oxidation and purification

For metal elimination (Fe^{3+}, Al^{3+}), about 0.5 g of sample was subjected to digestion with 10 ml of 4 M trifluoroacetic acid (TFA) for 4 hours at 105 °C in a high pressure digestion apparatus heated in an oven.

After the first digestion, the samples were collected by filtration through a glass fibre filter (GF 6, Schleicher and Schull, Dassel, Germany), rinsed several times with deionised water and dried at 30-40 °C for at least two hours. Thereafter, all of the residue was transferred to a glass digestion tube, 2 ml of 65% nitric acid (HNO_3) was added and the mixture was heated to 170 °C and held there for eight hours in the digestion apparatus, where black carbon was oxidised to BPCAs (Fig. 1).

The solution was poured through an ash-less cellulose filter (Schleicher and Schull 589[3], d = 70 mm) into a 10 ml volumetric flask. Deionised water was added to fill the flask. To eliminate

remaining polyvalent cations, an aliquot of 1.5 ml of the sample solution was diluted with 6 ml deionised water. Subsequently, 100 µl of the internal standard, phthalic acid was added (100 µg phthalic acid in 100 µl deionised water). The phthalic acid is an improvement on the original method (Brodowski et al., 2005), since this standard does not degrade as easily as citric acid originally used. The solution was then run over a column of cation exchange resin (Dowex 50 W X 8, 200-400 mesh, Fluka), which was converted to the H^+ form prior to use. The BPCA solutions were eluted into 100 ml conical flasks with 50 ml deionised water in portions of 10 ml. Finally, the eluates were freeze-dried to remove water.

Derivatisation

The freeze-dried BPCAs were re-dissolved in four times 1 ml methanol and transferred to 5 ml reactivials (Alltech GmbH), with Teflon-laminated septum screw caps. The dried BPCAs were converted to trimethylsilyl derivatives. For this purpose, we added 100 µl dry pyridine and 100 µl N,O-bis(trimelthylsilyl)-trifluoroacetamide (BSTFA), heated the solution at 80 °C for two hours, allowed it to cool and stored it for 24 hours.

Gas chromatography (GC)

GC analysis was performed with an Agilent 6890 gas chromatograph, equipped with a flame ionisation detector (FID) and an HP-5 capillary column (30 m x 0.32 mm i.d., 0.25 µm film thickness). Helium was used as carrier gas at a constant flow of 0.8 ml min^{-1}. Both the injector and detector temperatures were 300 °C. Aliquots (2 µl) of sample solution was injected at a split ratio of 30:1 into a fully deactivated inlet system with silylated liners. The temperature programme was: initial column temperature of 100 °C held for two minutes, followed by an increase of 20 °C min^{-1} to 240 °C and held for seven minutes. Subsequently, the temperature was raised by 30 °C min^{-1} to 300 °C and held for an additional 10 minutes.

Standard series

A standard series was prepared for each analysis run using standard solutions of 10, 15, 25, 50, 100 µg BPCA per vial (Fig. 1). The solution was prepared by dissolving 100 µg of each BPCA in 100 µl methanol and transferring the corresponding volume of standard solution into the vial. The internal standard, phthalic acid was added as 100 µg in 100 µl methanol. Subsequently, the standards were completely dried and individually derivatised as described above.

ACKNOWLEDGEMENTS

This PhD would not have been possible without the people mentioned on these two pages. Thank you, sincerely.

Michael Schmidt, the chef, who gave me the opportunity to do a PhD at the new Soil Biogeochemistry group he started at the university. He taught me a lot about asking questions and networking with people, both things that helped me a lot in my PhD.

Alex Heim, who shared an office with me until recently, whom I could always ask for help, be it a chemistry question, or something to do with the GC instrument; he was always willing to help. He also helped with my German writing (which is alas still appalling) and most recently helped to write the abstract in German in the front pages of this thesis.

Ron Smernik, whom I worked with on most of my papers – our NMR expert; without him my papers would all have been rejected, not only because of his clever scientific arguments, but also his perfect English.

Eileen Eckmeier, who was with me in this boat from the very first day in May 2003. We went on our first of many trips together to Bayreuth to learn the BPCA method just after we got here, and went through troubled and clear waters together during our years here. We had a great adventure in Russia in August 2004, as part of a Soil Science excursion, and shared rooms at conferences, although I was always up too early for her taste!

Sonja Brodowski, the mistress of the BPCA method, from whom I learnt how to master the method. She was always willing to help and answer endless questions.

Anett Hofmann, who joined our group almost two years ago. Her friendliness is contagious and she is always willing to help, like writing the German translation of the abstract in front of this thesis, and listening when I talked about my work.

Samuel Abiven, with his strange French style, giving advice about work (and wine), and always ready with a joke (although the rugby and cricket ones weren't always funny…). Bruno Kägi, for help in the laboratory and keeping me on my toes. Michael Hilf, for help in the laboratory and keeping everything so organised. Ottmar Joos, for friendly talks after a troubled start. Remo Zanelli, for interesting discussions about phantoms and the lot.

My friends and colleagues at 3G, those that are still here and those that have moved on, thank you for your friendship and help, and good times at and outside the University. Wilfried, you are a wonderful example for all of us. Perscheng, for all your help and interest.

Margaret Torn, for hosting me at the Lawrence Berkeley National Laboratory in Berkeley, California. I had a wonderful time there, learning many things and getting a different appreciation for Americans ☺

Caroline Masiello, for hosting me at Rice University for a very interesting meeting, and for agreeing to act as external examiner on this thesis.

The people who worked with me on the black carbon ring trial – all 41 of you. It was an enlightening experience from which I have learnt a great deal.

Ma en Pa, dankie vir julle ondersteuning en geloof in my, wat my tot hier gebring het, so ver van die huis af. Dankie dat julle hierdie prestasie vir my moontlik gemaak het, al het dis soos 'n berg gelyk om te doen. Ek waardeer dit eindeloos. En my broers en suster, dankie vir julle ondersteuning en kuiers en grappies. Julle is die beste.

My ander ma en pa, dankie vir julle ondersteuning en dat ek deel van julle gesin kon word. Dankie vir al die wonderlike kuiers, etes, en hulp. Ek waardeer dit baie.

Corrie, die beste vriendin wat mens voor kan vra. Ons het al soveel avonture gedeel, en ek hoop ons kan in die toekoms ook al is ons nie altyd op dieselfde kontinent nie. Ons deel 'n baie passievolle liefde vir die natuur – kriteria nommer 1 vir 'n beste vrirendin!

Mosh, my kat. Jy is wragtig die oulikste ding op aarde. Jy is die beste manier om my aandag van werk af te lei, iets was ook soms nodig was. En jou boetie, Kipp, wat iewers in die hemel ander diertjies help, het ook my hart so bly gemaak. En al my ander katjies, wat nog lewe en in die hemel is.

Frederik, my man, my beste vriend. Dankie dat jy my Switserland toe gebring het. Jy is die beste wetenskaplike wat ek ken. Ek waardeer al jou ondersteuning deur al die jare, goeie en slegte tye. Sonder jou sou ek nie hierdie selfopgelegde taak kon voltooi nie.

PART B

Characterisation and evaluation of reference materials for black carbon analyses using elemental composition, colour, BET surface area and ^{13}C NMR spectroscopy

Karen Hammes[a], Ronald J. Smernik[b], Jan O. Skjemstad[c], Michael W.I. Schmidt [a,1]

[a] *University of Zurich, Department of Geography, Winterthurstrasse 190, CH-8057, Zurich, Switzerland*
[b] *Soil and Land Systems, School of Earth and Environmental Sciences, University of Adelaide, Waite Campus, Urrbrae, SA 5064, Australia*
[c] *CSIRO Land and Water, Glen Osmond, Australia*

[1] Corresponding author: Fax: +41 44 635 6841
E-mail: michael.schmidt@geo.unizh.ch

Abstract

Different black carbon (BC) quantification methods usually lead to disparate results when the same sample is comparatively analysed. In many cases, this can be attributed to the physical and chemical properties of the sample. We describe herein a set of black carbon (BC) reference materials that can be used for calibration and comparison of BC quantification methods. The reference materials include three laboratory-produced BC-rich materials, five environmental BC matrices and four samples of non-BC organic matter that can potentially interfere with analysis. All the materials were chemically and physically characterised using elemental analyses, lightness measurements, BET surface area measurements and ^{13}C NMR analysis. The non-BC potentially interfering materials can lead to false positive data since they share properties with the BC-rich materials (high C-content, low lightness values and high aromaticity) that are used for certain BC quantification methods. The BC-rich materials represent two different sources of BC, namely a condensate from fossil fuel burning (soot) and residues from biomass burning (char), and are mainly distinguished from one another in chemical structure according to NMR observability and BET surface areas. The environmental matrices have relatively high amounts of inorganic matter and metal oxides, which have the potential to catalyse or inhibit thermal and chemical reactions during BC analysis. Having this standard set of well-characterised BC reference materials is a first step towards accurate quantification and understanding of the entire BC continuum.

1. Introduction

Black carbon (BC) is a term used to describe a range of carbonaceous materials produced during the incomplete combustion of biomass and fossil fuels. These materials display considerable variability in physical and chemical properties and can be described as a chemical continuum, ranging from submicron particles deposited from the gas phase as condensate (e.g. soot), to large residual pieces of charred plant material (Goldberg, 1985; Schmidt and Noack, 2000, Masiello, 2004). BC can be present in all kinds of environments, including the atmosphere, sediments and soils.

Numerous techniques have been employed to quantify BC and these can be divided into four categories: thermal, chemical, optical (as well as combinations of these three) and indirect methods (e.g. the formation of specific iron oxides and enhanced sorption affinity for polycyclic aromatic hydrocarbons; Schmidt and Noack, 2000). The most commonly applied methods are listed in Table 1. The BC determined by these methods is operationally defined and it is likely that most measure only a small range of the possible BC types formed. This means that data from measurements using different techniques are difficult to compare (Schmidt et al., 2001; 2003; Forbes et al., 2006; Preston and Schmidt, 2006; Hammes et al., in press). Furthermore, techniques are optimised for certain types of samples and matrices. For example, atmospheric scientists studying aerosols have developed methods with which to measure BC using the absorptivity of a sample

(Chughtai et al., 1998). This method probably cannot be applied to a highly absorptive matrix like soil or sediment without analytical modification.

The methodological problems in quantification have been highlighted in various comparative exercises, where results varied widely even on identical samples (Schmidt et al., 2001; Schmid et al., 2001; Currie et al., 2002; Schauer et al., 2003). As a result of these disparate results, a list of BC reference materials, divided into three sets, was compiled for use in an intercomparative study of methods determining BC in soils and sediments (Schmidt et al., 2003, Hammes et al., in press). The first set includes BC-rich materials produced in the laboratory (n-hexane soot, wood char, grass char; Hammes et al., 2006). The second includes non-BC materials that could potentially interfere with analysis (melanoidin, shale, bituminous coal, lignite coal). The third comprises environmental matrices that probably contain BC (urban aerosol, harbour marine sediment, two soils, dissolved organic matter). The advantages of these reference materials over some alternatives are that they are easily available, homogenous, inexpensive, and represent natural samples.

The set of BC reference materials was analysed in 17 laboratories via seven quantification methods (Table 1, Hammes et al., in press). Large systematic differences in BC content were found among the methods for all the materials. Two causes for these large differences were identified. First, each method detected, or was most sensitive for, different parts of the BC continuum. For example, the CTO-375 and sodium chlorite oxidation methods classified as BC virtually none of the carbon in the two laboratory-produced chars, whereas many of the other techniques classified virtually all of the carbon in these materials as BC. Second, it was recognised that there were a number of ways in which non-BC organic matter could be incorrectly measured as BC, or that BC could go undetected. Often this was ascribed to the effect of specific materials present in some of the samples on particular BC quantification methods. For example, protection of organic matter by the mineral matrix can reduce its susceptibility to oxidation and lead to its incorrect classification as BC in some methodologies. Although these factors were identified by Hammes et al. (in press), a thorough understanding of the factors requires a detailed chemical analysis of the reference materials. Furthermore, a key recommendation of the intercomparison study was that any BC quantification methodology developed in the future should be tested against the same set of reference materials. The existence of detailed chemical analysis of the reference materials would greatly assist in any such efforts.

In this paper we present, for the set of BC reference materials, chemical and physical properties (C, H, O, Fe and Al content, lightness, BET surface area and ^{13}C NMR spectra) that are important in a number of the BC quantification methodologies. We discuss (1) how the chemical and physical properties of the BC-rich materials may influence their detection using the various BC quantification methodologies, (2) whether the chemical and physical properties of the potentially interfering materials can explain their incorrect detection as BC with some of the BC quantification methodologies and (3) how the chemical and physical properties of the environmental matrices may have influenced the quantification of BC contained within them.

2. Experimental

2.1. Collection and preparation of BC reference materials

Laboratory-produced BC-rich materials

n-Hexane soot, produced under controlled laboratory conditions, from an *n*-hexane flame, was chosen as the soot standard. It is inexpensive to prepare, homogeneous and contains very few impurities like alkyl hydrocarbons (Akther et al., 1985; Smith and Chughtai, 1995). Samples were bottled in 1-gram quantities and stored in a dry, dark environment. The material was provided by D.M. Smith (University of Denver, USA). The wood and grass char were prepared at the Swiss Federal Laboratories for Materials Testing and Research (EMPA). The materials were pyrolysed at 450 °C for 5 hours (holding time) in a nitrogen atmosphere, after which they were ground and milled to a fine powder.

A detailed description of their production is reported in Hammes et al. (2006). The material (4-gram aliquots) was stored in a cool, dry place in aluminium containers and distributed by the University of Zurich.

Table 1. Summary of the most common BC quantification methods

Method	Principle
Chemo-thermal oxidation at 375 °C (Elmquist et al., 2004)	Sample oxidised at 375 °C for 18 h after acid pretreatment. Quantification of residual carbon as BC using elemental analysis.
Benzene polycarboxylic acid formation (Brodowski et al., 2005)	Sample oxidised in HNO_3 for 8 h after removal of polyvalent cations with acid, to form BPCAs from aromatic carbon. Quantification of BPCAs using GC/FID.
Acid dichromate oxidation (Song et al., 2002)	Sample oxidised in $K_2Cr_2O_7/H_2SO_4$ (varying timing) after acid pre-treatment. Quantification of residual carbon as BC using elemental analysis.
Thermal optical transmittance and reflectance (Schmid et al., 2001)	Sample heated stepwise to 900 °C under oxygen/helium air mixture. Quantification of residual carbon using laser transmittance or reflectance, followed by FID.
UV photooxidation (Skjemstad et al., 1999)	Sample photooxidised at 2.5 kW for 2 h in O_2-saturated water. Quantification of residual carbon as BC using ^{13}C NMR and elemental analysis.
Thermogravimetry coupled with differential scanning calorimetry (Lopez-Capel et al., 2005	Sample heated to 990 °C. Measures carbonaceous species being thermally oxidised while recording the mass difference recorded before and after heating.
Sodium chlorite oxidation (Simpson and Hatcher, 2004)	Sample oxidised (X3) with $NaClO_2$ for 4 h after acid pre-treatment. Quantification of residual carbon as BC using ^{13}C NMR and elemental analysis.

Non-BC potentially interfering materials

The two coals chosen as reference materials are typical end-members in coal maturity - namely a mature bituminous coal and an immature lignite coal. Pocahontas coal is a low-volatile bituminous coal, collected underground in Buchanan County (Virginia, USA) in June 1986. The lignite coal is from the Beulah Zap seam collected in Mercer County (North Dakota, USA). The high moisture content of this coal precluded processing through two successive stages of grinding. One half of the batch was processed for < 20-mesh material and the other half batch was ground just once to provide the < 100-mesh sample, which is used in this study (Vorres, 1990). The coals were acquired from the Argonne National Laboratory (Illinois, USA).

Green River shale samples were collected from the oil-rich Mahogany zone of the Green River Formation (Utah, USA). This shale is petroleum- and carbonate-rich and contains type I kerogen (Béhar and Vandenbroucke, 1987). The sample was acquired from the United States Geological Survey (USGS, Denver, USA).

Melanoidin was prepared by heating D-glucose (monohydrate) (100 g L^{-1}) and urea (10 g L^{-1}) in a 1:1 ratio (v:v) in glass jars at 90 °C for 30 days (stirred every second day). The brown residue was centrifuged, washed four times with deionised water and dried. This material was prepared and distributed by the University of Zurich.

Environmental BC matrices

The aerosol was acquired from the National Institute of Standards and Technology (NIST, Gaithersburg, USA) as standard reference material (SRM) 1649a, and is an atmospheric particulate material collected in the Washington DC area using a filter specially designed for the purpose. It supersedes SRM 1649 derived from the same batch of collected urban aerosol and includes data for new measurement parameters (Currie et al., 2002). The particulate matter was collected over a period of more than 12 months (1976-1977), and so represents a time-integrated sample. Details of the collection can be found in the certificate of analysis (NIST, 2001).

The marine sediment (SRM 1941b) was also acquired from NIST. This is the third issue of this marine sediment and was preceded by SRM 1941 and 1941a (NIST, 2004). The sediment was collected at the mouth of the heavily industrialised Baltimore Harbour in the Chesapeake Bay area (USA). This was the same site from which the sediments for SRM 1941 and 1941a were collected. Collection details can be found in the certificate of analysis (NIST, 2004).

Two soils containing substantial amounts of BC were chosen as reference materials – a clay soil (Vertisol) and a sandy soil (Chernozem).

The Vertisol (37% clay, 30% fine sand) was sampled in the region of Toowoomba (Queensland, Australia) at a depth of 0-10 cm (Schmidt et al., 2001). The Haplic Chernozem (19% clay, 53% fine sand) was sampled in the region of Hildesheim-Braunschweig at Harsum (northern Germany) at 20-60 cm depth, to minimise anthropogenic influence from ploughing and bomb ^{14}C. Both soils were treated with 50 KGy gamma radiation and stored in a cool, dry place. The soils were provided by J.O. Skjemstad (CSIRO Land & Water, Glen Osmond, Australia).

The dissolved organic matter (DOM) was collected from the Suwannee River (Georgia, USA) using reverse osmosis and is known as Suwannee River natural organic matter. For each sample, a 454 L aliquot of Suwannee River water was pre-filtered successively through 1-µm and 0.4-µm polypropylene filters and concentrated to about 8 L using a RealSoft PROS/2S portable reverse osmosis system. In brief, the samples were H^+-saturated, freeze dried, and homogenized. A detailed description of the isolation is contained in (Serkiz and Perdue, 1990). The material was acquired from the International Humic Substances Society (IHSS, University of Minnesota, USA).

2.2. Elemental analyses

Total C, H and N analysis for the calculation of the H/C and O/C molar ratios were carried out on a LECO CHN-900 instrument and O analysis on a LECO RO-478 instrument. For iron (Fe) and aluminium (Al) analyses by atomic absorbance spectroscopy (AAS), oven-dried samples were digested with a mixture of 2 mL HF (40%), 5 mL HCl (32%), 8 mL HNO_3 (65%) and 10 mL H_3BO_3 (5%).

2.3. Determination of lightness (L)

The colour of the reference materials, expressed as lightness (L), was determined with a spectrophotometer (Dr. Lange Spectro-color), d/8° with a 10 mm measuring aperture and SPECTRAL-QC computer software after calibration using the Dr. Lange black and white standards. The results are given in the colour-coordination system CIE L*a*b (L = lightness value; a = red value; b = yellow value). Only L-values are presented here, where a zero value represents no reflection and 100 total reflection.

2.4. BET surface area measurements

Nitrogen adsorption surface area measurements were performed at 77 K after drying (200 °C, 1 h) using the SA 3100 analyser (Coulter, USA). The apparent nitrogen surface area was calculated using the BET-equation for a pressure range p/p_0 0.0033 – 0.1.

2.5. Loss-on-ignition (LOI)

The method was done according to Nelson and Sommers (1996). Shortly, crucibles were heated in a muffle furnace at 400 °C for 2 h, cooled, and the tare weight determined to 0.1 mg. Duplicate samples of 1-3 g of air-dried, ground soil was added to a tarred crucible at heated to 105 °C for 24 h. The crucibles were cooled in a desicator and the weight of the crucibles plus samples determined. The weight of the over-dried samples was determined by subtraction. The samples were then ignited in a muffle furnace at 400 °C for 16 h. The crucibles were cooled and the weight of the crucible plus ignited sample determined. The weight of the samples were determined by subtraction. The LOI content of the sample was calculated as

$$\text{LOI, \%} = ((\text{Weight}_{105}-\text{Weight}_{400})/\text{Weight}_{105}) \times 100$$

Where "Weight_{105}" is weight of soil sample after heating at 105 °C and "Weight_{400}" is weight of soil sample after ignition at 400 °C.

2.6. Solid-state ^{13}C Nuclear Magnetic Resonance (NMR) spectroscopy

The aerosol, marine sediment, both soils and the shale were pre-treated with HF using the method of Skjemstad et al. (1994) prior to NMR analysis; all other samples were analysed without pre-treatment. Solid-state ^{13}C NMR spectra were obtained at a ^{13}C frequency of 50.3 MHz on a Varian Unity200 spectrometer (Varian, Palo Alta, CA) using both Cross Polarisation (CP) and Direct Polarisation (DP). Samples were spun at 5000 ± 100 Hz in a Doty Scientific MAS probe. The CP spectra were

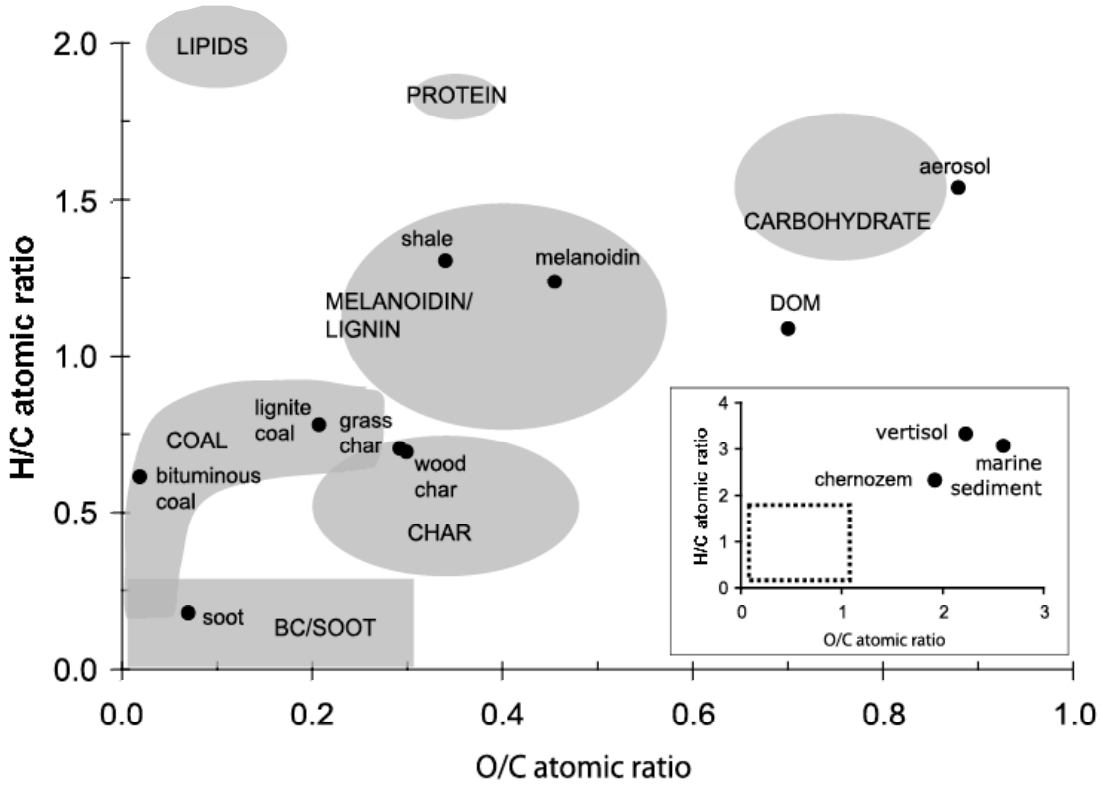

Fig. 1. Distinct groupings of individual biomolecular compounds (grey shading) for cellulose-rich material (carbohydrates), melanoidins, lignin (materials and monomers, charred materials (chars), different coals (coal) and soot. The groupings were adapted from Kim et al. (2003). The BC reference materials are plotted in relation to their H/C and O/C ratios and the grey shadings. Insert plot of Vertisol, Chernozem and marine sediment on another scale as the rest of the reference materials.

acquired using a one millisecond contact time and a recycle delay of between 0.5 s and 4 s. The DP spectra represent the accumulation of 1000 scans and were acquired using a 90 s recycle delay. Chemical shifts were externally referenced to the methyl resonance of hexamethylbenzene at 17.36 ppm. The distribution of signal in NMR spectra was quantified by integrating across four fixed chemical shift ranges: 210-165 ppm (designated as carbonyl C), 165-110 ppm (aryl C), 110-45 ppm (O-alkyl C) and 45-0 ppm (alkyl C). Signal in spinning sidebands (SSBs) was accounted for in the usual way, i.e. by integrating the low field carbonyl C and aryl C SSBs, which appear at chemical shifts 100 ppm higher than those of the corresponding central resonances (i.e. 310-265 ppm for carbonyl C and 265-210 ppm for aryl C), and adding twice this signal to that of the central bands, while subtracting this signal from that designated as O-alkyl C and alkyl C signal as appropriate. Spin counting experiments were performed using the method of Smernik and Oades (2000a) to determine the observability of carbon in the materials, i.e. how quantitative the spectra are. Errors in carbon NMR observabilities (C_{obs} values) are estimated to be ± 10% in C_{obs}-CP and ± 15% in C_{obs}-DP (Smernik and Oades, 2000a).

3. Results

3.1. Total carbon concentrations, atomic H/C and O/C ratios and metal oxides

The total carbon contents of the BC-rich materials and the potentially interfering materials are very similar, and all in excess of 500 g kg^{-1}, with the exception of shale (273 g kg^{-1} carbon) (Table 2). The environmental matrices all have lower C contents, although the aerosol and riverine DOM have relatively high carbon contents (177 g kg^{-1} C and 459 g kg^{-1} C respectively), compared to the two soils and the marine sediment (Table 2).

Van Krevelen diagrams are often used to compare the compositions of coals with regard to H/C and O/C atomic ratios (Killops and Killops,

2005), but can also give an indication of the degree of condensation of an organic material like char or shale. We adapted the groupings of individual biomolecular compounds displayed in Fig. 1 from Kim et al. (2003) to include not only lipids, protein, carbohydrates and coal, but also melanoidin, char and soot. The shale, soils, marine sediment and DOM do not have specific groupings. Although the total carbon contents of the soot, chars, coals and melanoidin were similar, their H/C and O/C atomic ratios plotted in distinguishable groupings on the van Krevelen diagram (Fig. 1). All the environmental matrices aerosol, soils, marine sediment), except the DOM, contain large amounts of mineral matter (Table 2). The high proportion of mineral matter (which contains H and O, but little or no C) and low C-contents of these materials affect their H/C and O/C ratios so that they plot well outside the range of the other reference materials (inset to Fig. 1).

Metal oxides present in a sample can catalyse or inhibit chemical and thermal reactions during analysis for certain methods. The soot and chars contain very little Fe and Al (<0.5 g kg^{-1}). The coals and melanoidin also contain little (< 5 g kg^{-1}) Fe and Al (Table 2). In contrast, the shale has high concentrations of Fe (20.9 g kg^{-1}) and Al (33.5 g kg^{-1}). All the environmental matrices (except the DOM) contain high concentrations of Fe (19.4-74.7 g kg^{-1}) and Al (32.8-82.5 g kg^{-1}).

3.2. Lightness values of reference materials

The BC-rich materials have low lightness values, similar to the potential interfering materials (L < 10), except shale (Table 2). The light colour of the shale (L = 44.4) distinguishes it and its organic matter (kerogen) from the BC-rich materials. The environmental materials are also lighter in colour (L = 15.4-53.5) compared to the other reference materials (except the shale). The lightness of the environmental matrices is roughly correlated with their carbon contents (R^2 = 0.7), despite the high amount of inorganic matter, since the aerosol and DOM have the highest carbon contents and the lowest colour values.

3.3. BET surface areas

The soot has a very high surface area compared to the wood char and grass char (73.9 m^{-2} g^{-1} vs. 2.0 and 5.9 m^{-2} g^{-1} respectively), underlining the differences in the structure of these BC materials (Hammes et al., 2006; Table 1). The potential interfering materials all have surface areas of less than 3.0 m^{-2} g^{-1}. The Vertisol has high surface area (57.3 m^{-2} g^{-1}), which reflects its high clay content (37%), making the material chemically and thermally reactive. The marine sediment also has a relatively high surface area (28.6 m^{-2} g^{-1}) compared to the other environmental matrices (Table 2).

3.4. Chemical structure of reference materials determined by cross polarisation and direct polarisation ^{13}C NMR signal intensities

Solid-state ^{13}C cross polarisation (CP) and direct polarisation (DP) NMR spectra of the reference materials are shown in Fig. 2. All of the BC-rich materials and potential interfering materials are highly aromatic. The solid-state CP ^{13}C NMR spectra of the soot and char materials show high signal intensities in the aryl-C region (71.7-77.7%) (Table 3); while the bituminous coal is similarly aromatic (82.5% aryl C). The DP signal intensities of these materials are in the same range (Table 3), and differences between their respective CP and DP spectra are minimal (Fig. 2b). The lignite coal and melanoidin also contain a reasonable proportion of aromatic C in the their CP spectra (55.2% and 32.0% aryl C respectively), but contain twice as much alkyl-C (22%) as the bituminous coal (11%). The kerogen has an alkyl-C signal intensity of 70% and an aryl-C signal intensity of about 15%, and can therefore be easily distinguished from BC-rich materials by NMR (Table 3). For each of the environmental matrices, apart from the DOM, their respective CP and DP spectra are substantially different (Fig. 2). In particular, in each case the DP spectrum contains substantially more signal in the aryl region than does the corresponding CP spectrum (Table 3). This can be explained by the low CP observability of charcoal C, relative to other types of organic matter present in these samples (Smernik and Oades, 2000a). For the aerosol sample, the alkyl signal is also enhanced in the DP spectrum relative to the CP spectrum. This indicates the presence of mobile alkyl C in this sample (Smernik and Oades, 2000b). In contrast, the CP and DP spectra of the

DOM are similar (Fig. 2), indicating that all C types are seen with similar efficiency by CP in this sample.

3.5. Observability of carbon in the reference materials

Quantification of C detection for both CP and BD spectra was gauged by spin counting, the results of which are shown in Table 3. The closer the NMR observability is to 100%, the more quantitative the spectra. Carbon NMR observabilities ranged from 6% to 80% for CP spectra and from 45% to 99% for DP spectra. The CP carbon observabilities for the soot and char materials are all low, but vary considerably from 6% for the soot to 40% for the grass char (Table 3). The DP observabilities for all three materials are much higher than the CP observabilities (Table 3). The DP observability for both of the chars is over 80%, indicating that these chars would not be substantially underestimated with respect to other organic matter types in DP spectra. The DP observability of 61% for the soot indicates that the soot would be moderately underestimated with respect to other organic matter types in DP spectra. Despite similar aromaticities, the CP observability is higher for the bituminous coal (56%) than for the chars (24-40%). The CP observability for the lignite coal is lower than for the bituminous coal, despite its lower aromaticity, indicating that aromaticity and the degree of aromatic condensation are not the only factors affecting observability. In the case of the lignite coal, we suggest that the low CP observability most likely results from paramagnetic interference. Both inorganic (this sample was not HF-treated) and organic (free radical) paramagnetic species can decrease NMR signal intensity. This proposition is supported by the short $T_{1\rho}H$ value recorded for this sample (2.13 ms, Table 3), and by the fact that its CP and DP spectra are similar in appearance (i.e. the DP spectrum is not more aromatic as is the case for the soils, sediment and aerosol).

4. Discussion

There are seven main BC quantification methods (Table 1). Method parameters, including oxidation time, temperature, and acid strength, determine largely what is actually measured as BC. However, the physical and chemical properties of the different materials also dictate how they will react when subjected to thermal and chemical oxidation. In the following sections, we discuss how the physical and chemical properties of the different reference materials influence their behaviour when analysed with different methods.

4.1. Laboratory-produced BC-rich materials

The BC-rich materials differed in a number of respects that are likely to affect BC quantification. The strongest contrast was between the soot and the two chars; differences between the two chars were generally quite small by comparison.

The soot had lower H/C and O/C ratios than the chars (Fig. 1), indicating a more condensed or graphitic structure. This should confer greater stability against thermal and chemical oxidation. Indeed, in the intercomparative study of Hammes et al. (in press), the CTO-375 and sodium chlorite methods (Table 1) were able to distinguish between the chars and the soot on this basis; the harsh oxidation steps used in these techniques effectively oxidised the chars to CO_2, but not the more resistant soot. The surface area of the soot was more than an order of magnitude greater than that of either of the two chars. This can be understood in terms of differences in their microstructure. Soot particles are formed at high temperatures (500-800 °C) in the gas phase as spheres (about 1 μm diameter), which cluster as grape-like structures, containing more than 90% carbon (Goldberg, 1985). This gives soot a very high surface area. Soot is also believed to have an outer shell consisting of singular carbon atom sheets (graphene), which limit oxygen transfer to the randomly structured inner core, protecting it from oxidation (Elmquist et al., 2006).

The chars for this study were produced at a much lower temperature that the soot (450 °C), which is thought to be a typical temperature of natural fires (Turney et al., 2006; Hammes et al., 2006). Chars formed at these lower temperatures are believed to have greater internal microporosity, allowing easier access for gases like oxygen during thermal oxidation. Nguyen et al. (2004) found that chars produced at higher temperatures (900-1000 °C) were more thermally recalcitrant than chars formed at lower temperatures (< 750 °C). Elmquist et al. (2006) demonstrated for the CTO-375 method (Table 1), that the carbon in the reference material chars was

not thermally stable at 375 °C and was completely oxidised, while the fraction of carbon remaining in the n-hexane soot after oxidation was 45.3%.

The higher DP observability compared to the CP observability for the BC-rich materials (Table 3) indicate very low hydrogen concentrations in these materials, which reduces the efficiency of the cross polarisation process during CP analysis. Once again, these values confirm that the soot is more condensed than the chars. The higher CP observability of the grass char (40%) compared to the wood char (24%) suggests a greater degree of aromatic condensation in the wood char. The BC-rich materials also have a number of properties in common, like high carbon contents, low lightness values and high aromaticity. However, these properties are not unique to BC-rich materials as discussed in the next section.

Non-BC potentially interfering materials

It is critical that BC quantification methods are able to distinguish between BC-rich materials and materials that share certain properties with them but do not have a pyrogenic origin. The melanoidin, shale, lignite coal and bituminous coal serve as models for materials that contain little or no BC, although all have properties similar to the BC-rich materials.

The melanoidin was chosen as a negative control for BC. It was not formed during combustion and thus cannot contain any BC. However, as it has a relatively high aromaticity and low lightness value, methods that use aromaticity or absorbtivity to measure BC, depend on the complete removal of melanoidin in a pre-treatment step to avoid melanoidin interference. Methods affected by this are the UV-photo oxidation method where NMR is employed, as well as thermal-optical transmittance and reflectance methods (discussed below) (Skjemstad et al., 1999; Schmid et al., 2001). Kerogen, represented here by the Green River shale, poses a potential problem for BC quantification due its stability against chemical oxidation. Techniques that only measure the amount of C remaining in the residue after oxidation, e.g. dichromate oxidation (Table 1), will quantify kerogen C that survives the degradative step as BC (Song et al., 2002).

On the other hand, techniques that include NMR characterization of the residue will not be adversely affected by the presence of organic matter such as found in the Green River shale, since it contains very little aromatic C.

It should be noted, however, that the chemical composition of kerogen varies greatly with maturity and with the composition of the aquatic organic matter from which it is derived. The Green River shale is a type I kerogen, and is derived from highly alkyl-rich starting material (Béhar and Vandenbroucke, 1987). It is immature, and so has not been subjected to the loss of alkyl C through oil generation, or to aromatising reactions. The potential for kerogen to interfere with BC quantification will be greater for more aromatic kerogens. Coals are formed by the same geological processes as kerogens, but generally from terrestrial organic matter rather than aquatic organic matter (Killops & Killops, 2005). This renders them more aromatic at similar degrees of maturity. Around 10% of the carbon in the bituminous coal investigated here is believed to be fossil charcoal (called inertinite) (Vorres, 1990), and could be potentially quantified as BC. The similarity of properties between the chars and the coal (and particularly the bituminous coal) presents problems for BC quantification. Given that the colour, H/C and O/C ratios, and the NMR spectra of the bituminous coal are all very similar to those of the BC-rich materials, ineffective removal of coal from an environmental sample in a pre-treatment step will mean that any coal remaining will be quantified as BC. This will lead to an overestimation of the contribution of BC to a specific environmental sample.

In the BC comparative exercise, most BC quantification methods could discriminate between the lignite coal and bituminous coal, since the bituminous coal is more recalcitrant to oxidation than the lignite coal (Hammes et al., in press). However for most of the techniques, most of the C in the bituminous coal was measured as BC. One property that did appear to distinguish the bituminous coal from the chars was CP observability. The CP observability of the bituminous coal C was 56% compared to 24-40% for the chars (Table 3). This suggests that the aromatic structures in the bituminous coal are less condensed.

Table 2. Elemental composition and colour of standard reference materials (n = 1 - 3)

Material	TC	N	H	O	Fe	Al	Ash*	Atomic ratio		Mass ratio	Lightness [e]	BET surface area [e]
	---------- g kg^{-1} ----------							H/C	O/C	C/N	L	m^{-2} g^{-1}
Laboratory produced BC-rich materials												
n-hexane soot	931 [a]	1.1 [a]	14.0 [a]	85.0 [a]	<0.1	0.1	34.9	0.2	0.1	854	0.1 ± 0.0	73.9
Chestnut wood char [b]	682	1.6	39.8	271	0.1	0.1	0.5	0.7	0.3	556	6.0 ± 0.4	2.0
Grass straw char [b]	586	12.4	34.7	227	0.5	0.2	192	0.7	0.3	49	5.7 ± 0.6	5.9
Non-BC potentially interfering materials												
Melanoidin	556	93.1	55.6	323	<0.1	0.2	2.5	1.2	0.5	6	8.1 ± 0.3	2.9
Shale	273	8.1	30.1	124	20.9	33.5	670	1.3	0.3	34	44.4 ± 0.1	0.8
Lignite coal	730 [c]	5.9 [c]	48.0 [c]	200 [c]	3.6	3.1	72.2	0.8	0.2	124	0.4 ± 0.1	1.6
Bituminous coal	859 [c]	11.9 [c]	44.0 [c]	20.0 [c]	4.9	4.8	25.8	0.6	0.0	72	9.2 ± 0.2	1.9
Environmental BC matrices												
Aerosol	177	26.9	23.3	210	35.7	32.8	620	1.5	0.9	7	15.4 ± 0.2	3.7
Marine sediment	31	2.0	8.2	109	74.7	82.5	893	3.1	2.6	16	53.5 ± 0.2	28.6
Vertisol	35	2.5	9.0	94.5	35.8	56.6	881	3.4	2.2	14	30.7 ± 0.2	57.3
Chernozem	20	1.5	3.8	49.1	19.4	43.5	933	2.4	1.9	11	32.0 ± 0.2	9.0
Dissolved organic matter	459 [d]	9.3 [d]	42.0 [d]	427 [d]	2.6	1.1	18.3	1.1	0.7	50	25.9 ± 0.1	-

*As determined by LOI
[a] Akhter et al., 1985
[b] All values from Hammes et al., 2006
[c] Vorres ,1990
[d] Huffman Laboratories, Wheat Ridge, CO, USA
[e] Hammes et al., in press

Table 3. Solid-state ^{13}C CP/DP NMR spectra signal intensity distribution and spin counting results of the BC reference material

	Carbonyl		aryl-C		O-alkyl		alkyl		$T_{1\rho}H$	C_{obs}(CP)	C_{obs}(DP)
ppm range	210-165		165-110		110-45		45-0		(ms)	(%)	(%)
	CP	DP	CP	DP	CP	DP					
Laboratory produced BC-rich material											
n-hexane soot	6.3	10.5	77.7	75.9	13.8	13.7	2.3	0.0	4.94	6	61
Chestnut wood char [a]	2.7	4.2	74.4	76.9	13.1	12.1	9.8	6.8	1.48	24	88
Grass straw char [a]	5.5	9.3	71.7	73.9	11.2	8.3	11.5	8.4	1.90	40	82
Non-BC potentially interfering materials											
Melanoidin	8.0	8.1	32.0	36.3	36.7	32.9	23.9	22.7	3.83	74	68
Shale [b]	1.0	2.2	15.1	18.8	11.8	14.8	72.1	64.4	4.20	80	98
Lignite coal	3.6	7.3	55.2	61.8	19.4	16.3	22.0	14.9	2.13	30	45
Bituminous coal	0.2	1.6	82.5	85.3	6.3	5.1	10.9	8.0	3.93	56	88
Environmental BC matrices											
Aerosol [b]	5.3	7.4	24.7	37.6	38.1	26.0	31.8	29.0	4.00	40	91
Marine sediment [b]	8.7	12.2	29.4	49.2	31.5	22.1	30.2	16.4	3.73	45	96
Vertisol [b]	12.1	14.5	39.0	53.0	32.4	23.1	16.5	9.7	3.54	55	88
Chernozem [b]	15.5	19.8	27.3	54.9	32.0	19.7	15.2	5.6	3.07	53	99
Dissolved organic matter	14.3	15.9	21.8	24.0	39.4	38.4	24.7	21.8	1.98	52	79

[a] All values from Hammes et al., 2006
[b] HF-treated

Environmental BC matrices

Measuring BC in environmental matrices may pose a considerable challenge. Not only is BC usually present in small amounts, there is also a large amount of organic matrix and minerals that can interfere with the quantification of BC in such a material.

The five environmental samples represent typical materials for which BC quantification is often sought, but do not necessarily span the variation within each type of material (Hammes et al., in press). In particular, the soils were specifically chosen to be "charcoal-rich". The BC in these samples comes from biomass burning (Skjemstad et al., 1997; Schmidt et al., 2001). The marine sediment and aerosol also believed to contain substantial quantities of BC, but in these cases it comes from fossil fuel burning, as these samples are sourced from an industrial harbour and an urban area (Currie et al., 2002; Mason et al., 2004). The DOM is the most different from the rest of the environmental matrices. It has a high carbon content, low aromaticity, low lightness value and a low ash content, which is mostly the opposite of the characteristics of the aerosol, marine sediment and the soils. The dominance of the inorganic matrix in the soils and sediment, and the corresponding low carbon contents, has some important methodological implications for BC quantification.

Firstly, H/C and O/C ratios, used to infer a degree of condensation and aromaticity in organic samples in a van Krevelen diagram (Fig. 1), are skewed by the presence of H and O in the mineral component. This is clearly seen for the soils and marine sediment, which plot well away from the organic materials in Fig. 1. The H/C and O/C ratios for these samples are clearly incompatible with purely organic structures.

Secondly, the lightness of the materials cannot be directly compared to those of the BC-rich materials, since the inorganic matrices contribute much to the lightness of the materials. However, Spielvogel et al. (2004) did report a correlation between colour and carbon content, and lightness and aromatic carbon content when comparing different soils with each other.

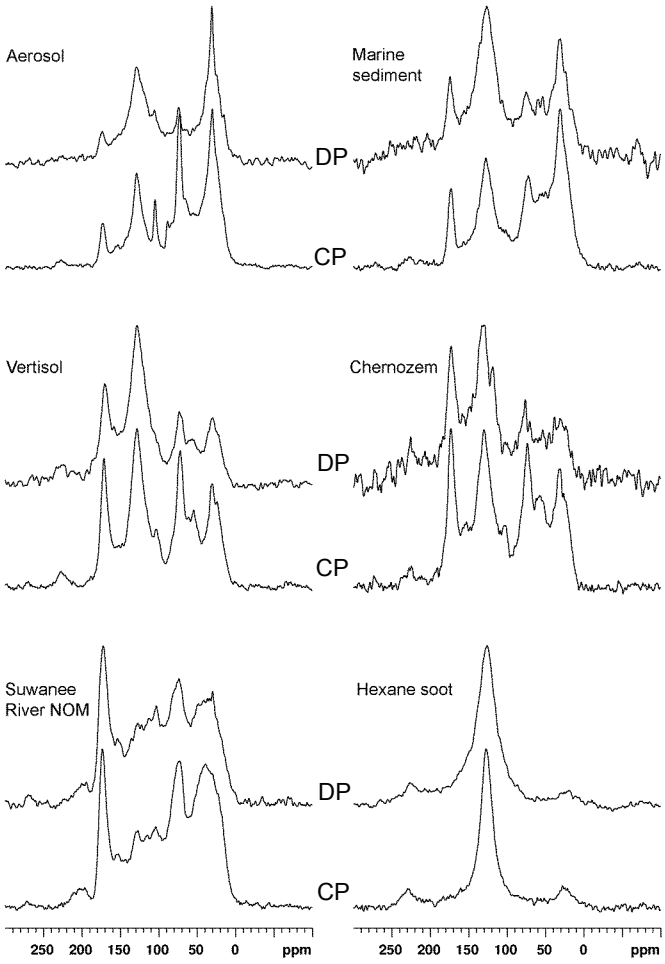

Fig. 2a. Solid-state ^{13}C NMR direct polarisation and cross polarisation spectra (top and bottom respectively) of the environmental BC matrices as well as the BC-rich hexane soot

Thirdly, the inorganic matrices may interfere in BC quantification, e.g. by catalysing or inhibiting reactions. The BPCA method is prone to this interference. In materials with a high amount of Fe and Al, the presence of these metals in a material could lead to the formation of organo-mineral complexes, which could interfere with the BPCA method and underestimate BC quantities (Glaser et al., 1998; Brodowski et al., 2005). Brodowski et al. (2005) have demonstrated that oxidised functional groups at the edges of BC structures make them prone to interactions with minerals. For the CTO-375 method, metal oxides act as catalysts, increasing the oxidation of the BC particles at a certain temperature, also leading to an underestimation of the BC content of a sediment (Elmquist et al., 2004). The nature of the minerals in the samples may influence the degree to which BC quantification is affected. For example, the high surface area of the Vertisol and the marine sediment make them potentially more prone to these effects.

Organic matrices can also create problems with BC quantification. Currie and Kessler (2005) evaluated the thermal optical transmission (TOT) method and the thermal optical kinetic (TOK) method for the isolation of BC (called elemental carbon (EC) in their paper) for micro-molar carbon accelerator mass spectrometry (AMS). A hybrid reference material was prepared consisting of forklift diesel soot (NIST SRM 2975), which is ^{14}C dead, and apple leaves (NIST SRM 1515), with a $^{14}C/^{12}C$ ratio of the living biosphere. Results showed significant contamination from the apple leaf biomass carbon in the BC fraction for both methods, where the split between organic carbon and resistant BC is wrongly appointed.

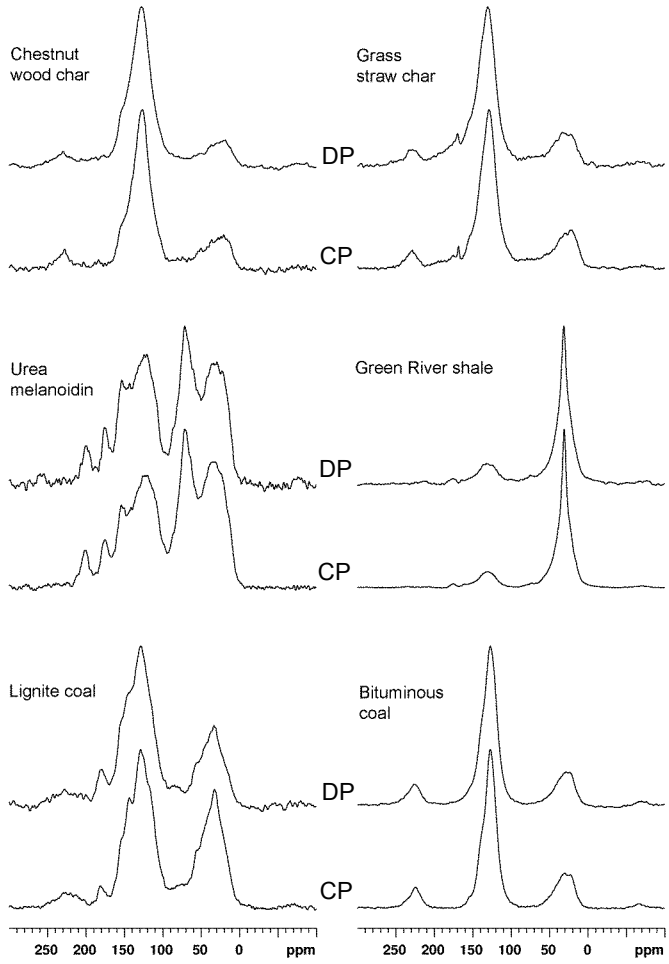

Fig. 2b. Solid-state ^{13}C NMR direct polarisation and cross polarisation spectra (top and bottom respectively) of the BC-rich chars (Hammes et al., 2006) and the non-BC potentially interfering materials

In an extensive inter-laboratory comparison (18 teams) of BC quantification using thermal-optical methods in the same aerosol that is part of the BC reference materials, charring of the non-BC organic matter was found to be a problem (Currie et al., 2002). This implies that methods that do not correct for charring will overestimate the amount of BC present. Most thermal-optical methods apply charring corrections, and the accuracy of this should be carefully monitored (Schmid et al., 2001; Schauer et al., 2003). When a sample has a low lightness value, the absorption is such that an additional blackening by charring during heating cannot be discriminated from the original absorption signals (Schmid et al., 2001).

Summary and conclusions

- The non-BC potentially interfering materials can lead to false positive data since they share properties with the BC-rich materials (high C-content, low lightness values and high aromaticity) that are used for certain BC quantification methods.
- The BC-rich materials represent two different sources of BC, namely a condensate from fossil fuel burning (soot) and residues from biomass burning (char). They are mainly distinguished from one another in chemical structure, where the CP observability of the soot is much lower, and the BET surface area much higher than that of the chars.
- The environmental matrices have relatively high amounts of inorganic matter and metal

oxides, which have the potential to catalyse or inhibit thermal and chemical reactions during BC analysis.

- Given these potential pitfalls and differences in chemical and thermal reactivity of materials, we strongly recommend that future BC studies include calibration of all methods against the set of BC reference materials presented here. Using these same materials for future methodological improvements and development of novel analytical approaches to quantify BC in environmental samples could prove to be invaluable in creating standard results that will be comparable.

Acknowledgements

The elemental analyses were done by Bruno Kägi (University of Zurich) and Michael Schneider (Swiss Technical University, ETH). Andreas Herzog and Anke Broenstroep (EMPA) did the BET analyses.

References

Akhter, M.S., Chughtai, A.R., Smith, D.M. (1985) The structure of hexane soot I: Spectroscopic studies. Applied Spectroscopy 39, 143-153.

Béhar, F., Vandenbroucke, M. (1987) Chemical modelling of kerogen. Organic Geochemistry 11, 15-24.

Brodowski, S., Amelung, W., Haumaier, L., Abetz, C., Zech, W. (2005) Morphological and chemical properties of black carbon in physical soil fractions as revealed by scanning electron microscopy and energy-dispersive X-ray spectroscopy. Geoderma 128, 116-129.

Brodowski, S., Rodionov, A., Haumeier, L., Glaser, B., Amelung, W. (2005) Revised black carbon assesment using benzene polycarboxylic acids. Organic Geochemistry 36, 1299-1310.

Chughtai, A.R., Atteya, M.M.O., Kim, J., Konowalchuk, B.K., Smith, D.M. (1998) Adsorption and adsorbate interaction at soot particle surfaces. Carbon 36, 1573-1589.

Currie, L.A., Benner, J.B.A., Kessler, J.D., Klinedinst, D.B., Klouda, G.A., Marolf, J.V., Slater, J.F., Wise, S.A., Cachier, H., Cary, R., Chow, J.C., Watson, J., Druffel, E.R.M., Masiello, C.A., Eglinton, T.I., Pearson, A., Reddy, C.M., Gustafsson, O., Hartmann, P.C., Quinn, J.G., Hedges, J.I., Prentice, K.M., Kirchstetter, T.W., Novakov, T., Puxbaum, H., Schmid, H. (2002) A critical evaluation of interlaboratory data on total, elemental, and isotopic carbon in the carbonaceous particle reference material, NIST SRM 1649a. Journal of Research of the National Institute of Standards and Technology 107, 279-298.

Currie, L.A., Kessler, J.D. (2005) On the isolation of elemental carbon (EC) for micro-molar ^{14}C accelerator mass spectrometery: development of a hybrid reference material for ^{14}C-EC accuracy assurance, and a critical evaluation of the thermal optical kinetic (TOK) EC isolation procedure. Atmospheric Chemistry and Physics 5, 2833-2845.

Elmquist, M., Gustafsson, Ö., Andersson, P. (2004) Quantification of sedimentary black carbon using the chemothermal oxidation method: an evaluation of ex situ pretreatments and standard additions approach. Limnology and Oceanography 2, 417-427.

Elmquist, M., Cornelissen, G., Kukulska, Z., Gustafsson, Ö. (2006) Distinct oxidative stabilities of char versus soot black carbon: Implications for quantification and environmental recalcitrance. Global Biogeochemical Cycles 20, GB2009, doi:10.1029/2005GB002629.

Forbes, M.S., Raison, R.J., Skjemstad, J.O. (2006) Formation, transformation and transport of black carbon (charcoal) in terrestrial and aquatic ecosystems. Science of the Total Environment 370, 190-206.

Glaser, B., Haumaier, L., Guggenberger, G., Zech, W. (1998) Black carbon in soils: the use of benzenecarboxylic acids as specific markers. Organic Geochemistry 29, 811-819.

Goldberg, E.D. (1985) Black Carbon in the Environment. John Wiley & Sons Inc., New York.

Hammes, K., Smernik, R.J., Skjemstad, J.O., Herzog, A., Vocht, U.F., Schmidt, M.W.I. (2006) Synthesis and characterisation of laboratory-charred grass straw (*Oryza sativa*) and chestnut wood (*Castanea sativa*) as reference materials for black carbon quantification. Organic Geochemistry 37, 1629-1633.

Hammes, K., Schmidt, M.W.I., Smernik, R.J., Currie, L.A. (Ret.), Ball, W.P., Nguyen, T.H., Louchouarn, P., Houel, S., Gustafsson, Ö., Elmquist, M., Cornelissen, G., Skjemstad, J.O., Masiello, C.A., Song, J., Peng, P., Mitra, S., Dunn, J.C., Hatcher, P.G., Hockaday, W.C., Smith, D.M., Hartkopf-Fröder, C., Böhmer, A., Lüer, B., Huebert, B.J., Amelung, W., Brodowski, S., Huang, L., Zhang, W., Gschwend, P.M., Flores-Cervantes, D.X., Largeau, C., Rouzaud, J.-N., Rumpel, C., Guggenberger, G., Kaiser, K., Rodionov, A., Gonzalez-Vila, F.J., Gonzalez-Perez, J.A., de la Rosa, J.M., Manning, D.A.C., López-Capél, E., Ding, L. (accepted). Comparison of black carbon quantification methods to measure fire-derived (black/elemental) carbon in soils and sediments using reference materials from

soil, water, sediment and the atmosphere. Global Biogeochemical Cycles, in press.

Killops, S.D., Killops, V.J. (2005) An Introduction to Organic Geochemistry. Blackwell Science Ltd.

Kim, S., Kramer, R.W., Hatcher, P.G. (2003) Graphical method for analysis of ultrahigh-resolution broadband mass spectra of natural organic matter, the van Krevelen diagram. Analytical Chemistry 75, 5336-5344.

Lim, B., Cachier, H. (1996) Determination of black carbon by chemical oxidation and thermal treatment in recent marine and lake sediments and Cretaceous-Tertiary clays. Chemical Geology 131, 143-154.

Lopez-Capel, E., Sohi, S.P., Gaunt, J.L., Manning D.A.C. (2005) Use of thermogravimetry-differential scanning calorimetry to characterize modelable soil organic matter fractions. Soil Science Society of America Journal 69(1), 136-140.

Masiello, C.A. (2004) New directions in black carbon organic geochemistry. Marine Chemistry 92, 201-213.

Mason, R.P., Kim, E.-H., Cornwell, J. (2004) Metal accumulation in Baltimore Harbor: current and past inputs. Applied Geochemistry 19, 1801-1825.

Nelson, D.W., Sommers, L.E. (1996) Total carbon, organic carbon and organic matter. In: Bartels (ed.) Methods of Soil Analysis Part 3: Chemical Methods, p. 1004 – 1005.

Nguyen, T.H., Brown, R.A., Ball, W.P. (2004) An evaluation of thermal resistance as a measure of black carbon content in diesel soot, wood char, and sediment. Organic Geochemistry 35, 217-234.

NIST (2001) Certificate of analysis, Standard Reference Material (SRM) 1649a, Urban dust. National Institute of Standards and Technology, Gaithersburg, MD.

NIST (2004) Certificate of Analysis, Standard Reference Material (SRM) 1941b, Organics in marine sediment. National Institute of Standards and Technology, Gaithersburg, MD.

Preston, C.M., Schmidt M.W.I. (2006) Black (pyrogenic) carbon: a synthesis of current knowledge and uncertainties with special consideration of boreal regions, Biogeoscience *3*, 397-420.

Schauer, J.J., Mader, B.T., Deminter, J.T., Heidemann, G., Bae, M.S., Seinfeld, J.H., Flagan, R.C., Cary, R.A., Smith, D., Huebert, B.J., Bertram, T., Howell, S., Kline, J.T., Quinn, P., Bates, T., Turpin, B., Lim, H.J., Yu, J.Z., Yang, H., Keywood, M.D. (2003) ACE-Asia intercomparison of a thermal-optical method for the determination of particle-phase organic and elemental carbon. Environmental Science & Technology 37, 993-1001.

Schmid, H., Laskus, L., Abraham, H.J., Baltensberger, U., Lavanchy, V., Bizjak, M., Burba, P., Cachier, H., Crow, D., Chow, J., Gnauk, T., Even, A., Ten Brink, H.M., Giesen, K.-P., Hitzenberger, R., Hueglin, C., Maenhaut, W., Pio, C., Carvalho, A., Putaud, J.-P., Toom-Sauntry, D., Puxbaum, H. (2001) Results of the "carbon conference" international aerosol carbon round robin test stage I. Atmospheric Environment 35, 2111-2121.

Schmidt, M.W.I., Noack, A.G. (2000) Black carbon in soils and sediments: Analysis, distribution, and current challenges. Global Biogeochemical Cycles 14, 777-794.

Schmidt, M.W.I., Skjemstad, J.O., Czimczik, C.I., Glaser, B., Prentice, K.M., Gelinas, Y., Kuhlbusch, T.A.J. (2001) Comparative analysis of black carbon in soils. Global Biogeochemical Cycles 15, 163-167.

Schmidt, M.W.I., Masiello, C.A., Skjemstad, J.O. (2003) Final recommendations for reference materials in black carbon analysis. EOS, Transactions, American Geophysical Union 84(52), 582-583.

Serkiz, S.M., Perdue, E.M. (1990) Isolation of dissolved organic matter from the Suwannee River using reverse osmosis. Water Research 24, 911-916.

Simpson, M.J., Hatcher, P.G. (2004) Determination of black carbon in natural organic matter by chemical oxidation and solid state 13C nuclear magnetic resonance spectroscopy. Organic Geochemistry 35, 923-935.

Skjemstad, J.O., Clarke, P., Taylor, J.A., Oades, J.M., Newman, R.H. (1994) The removal of magnetic materials from surface soils. A solid state ^{13}C CP/MAS n.m.r. study, Australian Journal of Soil Research 32, 1215-1229.

Skjemstad, J.O., Clark, P., Golchin, A., Oades, J.M. (1997) Characterization of soil organic matter by solid state ^{13}C NMR spectroscopy. In: G. Cadisch, K. Giller (Eds.), Driven by Nature: Plant Litter Quality and Decomposition. Cab International, pp. 253-271.

Skjemstad, J.O., Taylor, J.A., Smernik, R.J. (1999) Estimation of charcoal (char) in soils. Communications in Soil Science and Plant Analysis 30, 2283-2298.

Smernik, R.J., Oades, J.M. (2000a). The use of spin counting for determining quantitation in solid state ^{13}C NMR spectra of natural organic matter. 1. Model systems and the effects of paramagnetic impurities. Geoderma 96, 101-129.

Smernik, R.J., Oades, J.M. (2000b). The use of spin counting for determining quantitation in solid state ^{13}C NMR spectra of natural organic matter. 2. HF-treated soil fractions. Geoderma 96, 159-171.

Smith, D.M., Chughtai, A.R. (1995) The surface structure and reactivity of black carbon. Colloids and Surfaces A 105, 47-77.

Song, J., Peng, P., Huang, W. (2002) Black carbon and kerogen in soils and sediments. 1. Quantification and characterization. Environmental Science & Technology 36, 3960-3967.

Spielvogel, S., Knicker, H., Kögel-Knabner, I. (2004) Soil organic matter composition and soil lightness. Journal of Plant Nutrition and Soil Science 167, 545-555.

Turney, C.S.M., Wheeler, D., Chivas, A.R. (2006) Carbon isotopic fractionation in wood during carbonization. Geochimica et Cosmochimica Acta 70, 960-964.

Vorres, K. (1990) The Argonne Premium Coal Sample Program. Energy & Fuels 4, 420-426.

Available online at www.sciencedirect.com
ScienceDirect
Organic Geochemistry 37 (2006) 1629–1633
Organic Geochemistry
www.elsevier.com/locate/orggeochem

Note

Synthesis and characterisation of laboratory-charred grass straw (*Oryza sativa*) and chestnut wood (*Castanea sativa*) as reference materials for black carbon quantification

Karen Hammes [a], Ronald J. Smernik [b], Jan O. Skjemstad [c], Andreas Herzog [d], Ulrich F. Vogt [d], Michael W.I. Schmidt [a,*]

[a] *University of Zurich, Department of Geography, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland*
[b] *Soil and Land Systems, School of Earth and Environmental Sciences, University of Adelaide, Waite Campus, Urrbrae, SA 5064, Australia*
[c] *CSIRO Land and Water, Glen Osmond, Australia*
[d] *EMPA Materials Science and Technology, Laboratory for High Performance Ceramics, Ueberlandstrasse 129, CH-8600 Dübendorf, Switzerland*

Received 1 March 2006; received in revised form 28 June 2006; accepted 4 July 2006
Available online 7 September 2006

Abstract

We synthesised large (~2 kg) quantities of two chars for use as commercially available reference materials for the quantification of black carbon (BC). We pyrolysed chestnut wood (*Castanea sativa*) and grass straw (*Oryza sativa*) at 450 °C under a N_2 atmosphere, which mimics the oxygen-free conditions on the inside of burning material at a moderate burning temperature. The charred materials were dominated by aromatic carbon (~70%), had low H/C (~0.7) and O/C (~0.3) ratios and low surface areas (2–6 $m^2\ g^{-1}$). Isotopic changes on charring were small (≤0.3‰). In these respects, the synthesised chars were similar to chars produced at low temperature (<500 °C) in natural fires and thus may prove to be appropriate materials for calibrating BC quantification methods. Both chars have been used in a comparative study of BC quantification.

1. Introduction

Methods that can reliably quantify BC in various matrices are needed to provide more accurate global carbon budget assessments, air pollution inventories and fire history reconstructions (Kuhlbusch, 1998). The development and testing of BC quantification methods would benefit from well characterised char reference materials, to aid in the understanding of the disparate results obtained from different quantification methods (Schmidt et al., 2003). While soot (formed at higher temperature) is commercially available as a reference material, char from low temperature natural biomass burning is not. For this purpose we synthesised chars at 450 °C, a typical temperature for natural fires (Turney et al., 2006) and covering the lower temperature end of BC production. Producing the chars under exact laboratory

* Corresponding author. Fax: +41 44 635 6848.
E-mail address: mschmidt@geo.unizh.ch (M.W.I. Schmidt).

0146-6380/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.orggeochem.2006.07.003

conditions ensures that these materials can be reproduced in the future. To our knowledge this is the first detailed characterisation of wood and grass char produced specifically for use as BC reference materials. They are available from our laboratory. They have been used in a comparative study of BC quantification (http://www.geo.unizh.ch/phys/bc).

In this study, we (1) provide detailed characterisation of two chars produced under controlled conditions, (2) compare them with other artificial and natural chars (where burning conditions are often unknown) and (3) assess their suitability as reference materials.

2. Experimental

The chestnut wood (*Castanea sativa*) originated from a single tree in a forest in southern Switzerland (Ticino, between Bedano and Gorduno, 530 masl). The grass straw (*Oryza sativa* L. cv Arborio) also originated from southern Switzerland (Ticino, between Locarno and Ascona, 197 masl) from a commercial rice farm (Terreni alla Maggia SA, CH-6612 Ascona). The materials were not further dried before charring. Debarked and cut chestnut wood ($40 \times 5 \times 5$ cm) and bundled grass straw were charred in a GERO GLO 40/11 pyrolysis oven (Neuhausen, Germany; 0.8 m × 0.31 m diameter), under a N_2 atmosphere (flow 500 L h^{-1}). The temperature was raised from room temperature to 200 °C (300 K h^{-1}) and then to 450 °C (50 K h^{-1}), at which it was held for 5 h to achieve a constant weight. The charcoal was collected after cooling (8 h), crushed in a mechanical crusher and milled in a ball mill to a fine powder. The material was stored in a cool, dry place in aluminium containers. Samples were weighed before and after pyrolysis to determine mass loss. The ash content was determined using the loss on ignition (LOI) method where samples are dried at 105 °C for 24 h and ignited at 400 °C for 16 h.

Solid state ^{13}C NMR spectra were obtained at a ^{13}C frequency of 50.3 MHz with a Varian Unity 200 spectrometer using cross polarisation (CP) and Direct Polarisation (DP). Samples were spun at 5 kHz. For the CP spectra a 1 ms contact time was used. The recycle delay was 4 s for the uncharred samples and 1 s for the charred samples; 1000 scans were collected for the uncharred samples and 4000 for the charred samples. For the DP spectra a total of 1000 scans was collected with a recycle delay of 90 s. Chemical shifts were externally referenced to the methyl resonance of hexamethylbenzene at 17.36 pm.

Stable carbon isotope ($\delta^{13}C$) values were determined by Iso-Analytical Ltd. (Sandbach, UK) using a Europa Scientific 20–20 isotopic ratio mass spectrometer (EA-IRMS). Total C, H and N analysis for calculation of H/C and O/C molar ratios were carried out with a LECO CHN-900 instrument and O analysis with a LECO RO-478 instrument.

Nitrogen adsorption surface area measurements were performed at 77 K after drying (200 °C, 1 h) using a SA 3100 analyser (Coulter, USA). The apparent nitrogen surface area was calculated using the BET equation for a pressure range p/p_0 0.0033 – 0.1.

3. Results and discussion

3.1. Characterisation of wood and grass char materials

The H/C and O/C ratios of the wood and grass decreased on charring, as reported in previous studies in which biomass (peas, peat and sapwood) was subjected to different degrees of heating (Baldock and Smernik, 2002; Almendros et al., 2003; Braadbaart et al., 2004). A van Krevelen plot of H/C versus O/C (Fig. 1) is a convenient way to visualising the changes. Three steps are characteristic of condensation to form a carbon-rich product: (1) initial dehydration; (2) dehydrogenation and demethylation (loss of CH_3); (3) decarboxylation (loss of CO_2) and demethylation (see insert in Fig. 1; Bal-

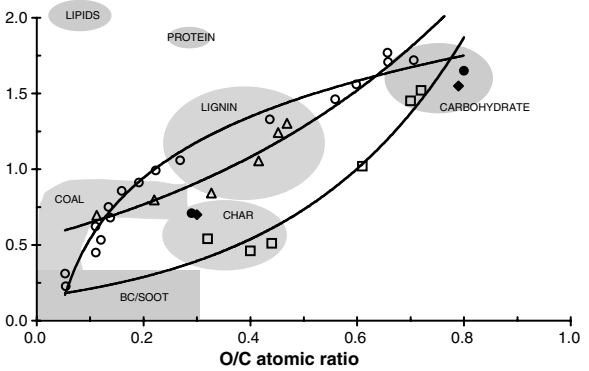

Fig. 1. Processes related to charring of biomass: wood (filled diamonds) and grass straw (filled circles), before and after charring. Heating of other biomass materials: peas (open circles, Braadbaart et al., 2004), peat (open triangles, Almendros et al., 2003) and sapwood (open squares, Baldock and Smernik, 2002). Grey shadings = areas of biomolecular components (adapted from Kim et al., 2003).

dock and Smernik, 2002; Kim et al., 2003; Braadbaart et al., 2004). The H/C and O/C ratios of the wood and grass char were almost identical. However, we suspect that the grass char (and grass straw) picked up some water, increasing the H/C and O/C ratios. Generally, H/C and O/C ratios of chars differ, depending on the type of material, the heating atmosphere and temperature of formation (intensity of heating) as illustrated by the different charred biomass in Fig. 1.

Carbon-13 CP and DP MAS NMR spectra are shown in Fig. 2. Only CP spectra were recorded for the uncharred materials since the CP "observability" for the wood and grass was 99% and 93% respectively. The distribution of signals in the spectra are presented in Table 1. The spectra of both the wood and the grass before charring were dominated by signals in the O-alkyl C region (45–110 ppm), reflecting the dominance of cellulose (Preston et al., 1998; Baldock and Smernik, 2002). A methoxyl carbon signal at 56 ppm and several signals in the aryl C region (165–110 ppm) were stronger for the wood than for the grass, reflecting a higher content of lignin and/or presence of hydrolysable tannin in the wood. Weak signals were present in the alkyl (0–45 ppm) and carboxyl (210–165 ppm) regions.

The CP and DP spectra of both materials after charring were similar, being dominated by peaks in the aryl region (110–165 ppm). The aryl peak was centred at 126.5 ppm in the CP spectrum and 127.3 ppm in the DP spectrum for the wood char, and at 128.8 ppm in the CP spectrum and 129.3 ppm in the DP spectrum for the grass char. Both chars contained 10–15% of the signal in each of the alkyl (0–45 ppm) and O-alkyl (45–110 ppm) regions (Table 1), indicating that not all the C was transformed into condensed aryl structures. However, it should be noted that around half of this signal could be attributed to signal from the aromatic spinning sidebands. The DP "observability" for the wood char was 88% and for the grass char 82%, while the CP "observability" was 24% and 40% respectively.

Both char spectra contained shoulders in the O-aryl region (160 ppm), which might be attributable to remaining lignin structures, or newly formed compounds, such as benzo-furans, polycyclic aromatic hydrocarbons or heterocyclic compounds (Baldock and Smernik, 2002). The small peak at 168 ppm in the grass char spectrum could indicate the presence of small amounts of carboxylic acid (attached to aryl rings) or bicarbonate in the alkaline ash.

The ash content was much less for wood ($\sim$1 g kg^{-1}) than for grass (77 g kg^{-1}, Table 1), as expected (Krull et al., 2003). Mass recovery (wood

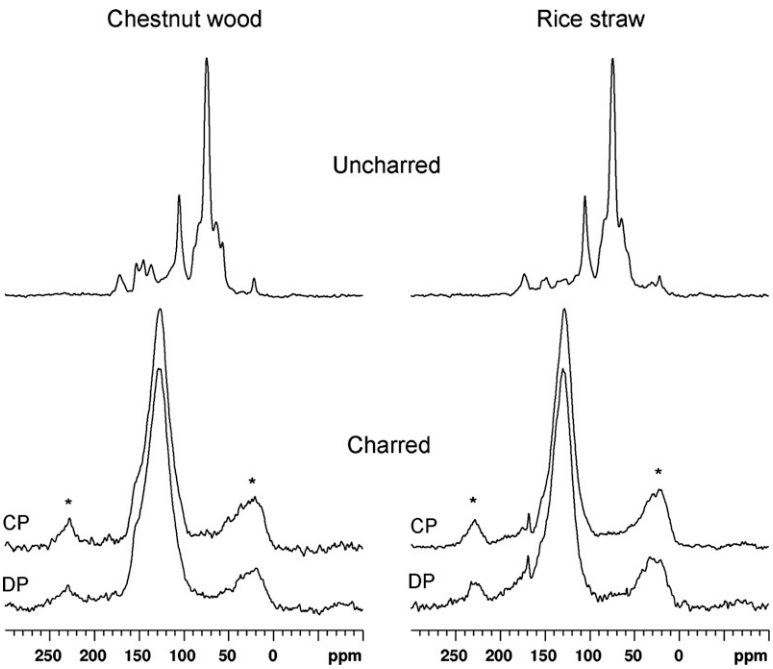

Fig. 2. ^{13}C NMR CP and DP spectra of wood and grass straw, before and after charring; *indicates spinning sidebands.

Table 1
Isotopic, elemental composition and CP and DP NMR signal intensities of wood and grass before and after charring ($n = 1$–2)

Reference material	Mass (%) [a]	C (g kg^{-1})	N (g kg^{-1})	H (g kg^{-1})	O (g kg^{-1})	Atomic ratio		Mass ratio	δ-^{13}C (‰(V-PBD))	Mineral matter[b] (g kg^{-1})	BET surface area (m^2 g^{-1})	% Total acquired NMR signal (ppm)							
						H/C	O/C	C/N				Carboxyl C (210–165 ppm)		Aryl C (165–110 ppm)		O/N-Alkyl C (110–45 ppm)		Alkyl C (45–0 ppm)	
												CP	DP	CP	DP	CP	DP	CP	DP
Wood		457.7	0.7	59.4	479.7	1.6	0.8	920	−26.6	0.8	–	3.8	–	21.8	–	72.8		1.7	–
Wood char		682.0	1.6	39.8	270.6	0.7	0.3	690	−26.9	0.5	2.0	2.7	4.2	74.4	76.6	13.1	12.1	9.8	6.8
Recovery (%)	40	59	98	27	23														
Grass		422.7	6.2	58.7	452.9	1.7	0.8	64	−26.4	76.8	–	4.9	–	13.6	–	75.6	–	5.9	–
Grass char		586.3	12.4	34.7	227.0	0.7	0.3	49	−26.5	191.5	5.9	5.5	9.3	71.7	73.9	11.2	8.3	11.5	8.4
Recovery (%)	35	49	71	21	18														

[a] Mass recovery after pyrolysis in mass%.
[b] Mineral matter (ash) determined by LOI.

40%, grass 35%) were similar to those previously reported for pyrolysis residues formed at 450–480 °C under an inert atmosphere (mass recovery 20–30%; Czimczik et al., 2002; Brown et al., 2006). Recovery of initial carbon was 49% for grass and 59% for wood after pyrolysis. Due to the preferential loss of H and O with heating, carbon concentration and degree of aromatisation typically increased with pyrolysis. Mass recovery of the initial nitrogen was 71% for grass and 98% for wood (Table 1). This is consistent with decreasing C/N ratio values on charring, indicating that nitrogen is preferentially preserved (Almendros et al., 2003).

Stable C isotope ratio values for the chestnut wood (−26.6‰) and grass (−26.4‰) were typical for many C_3 plants (Krull et al., 2003), with minor depletion ($\leqslant$ 0.3‰) on charring (Table 1). Isotopic depletion in ^{13}C also took place in other wood types after heating to temperatures between 150 °C and 480 °C (Czimczik et al., 2002; Turney et al., 2006).

The surface area of the chars (< 10 m^2 g^{-1}) was similar to that found for pitch pine char produced at a final temperature of 450 °C, and less than that produced at higher temperature (> 500 °C, 250–340 m^2 g^{-1}; Brown et al., 2006).

3.2. Comparison with other laboratory-produced and natural chars

Several studies report laboratory-produced char, but only a few report elemental (H, C, N, O) concentrations and specific surface area (no isotopic (δ^{13}C) information) for the same samples (11 out of 44 individual chars) formed between 70 and 1000 °C (Baldock and Smernik, 2002; Czimczik et al., 2002; Nguyen et al., 2004; Zhu et al., 2005; Brown et al., 2006; Turney et al., 2006). The final formation temperature and gas composition during heating influence char properties (Brown et al., 2006). For natural chars, the temperature of formation is difficult to measure and is rarely known. Thus, parameters like H/C ratio, specific surface area and δ^{13}C value could help infer the temperature of formation of natural chars. Interestingly, an H/C atomic ratio > 0.5 seems to indicate chars which experienced temperatures < 500 °C, whereas chars with H/C < 0.5 were mostly formed at higher temperature (500–1000 °C). Additionally, these low temperature chars generally had low surface area (< 25 m^2 g^{-1}), whereas high temperature chars generally had large surface area (214–336 m^2 g^{-1}), except

when temperature ramping was slow ($< 0.5\ m^2\ g^{-1}$, 30–200 °C h^{-1}). Low temperature chars also had a high surface area when exposed to oxygen during heating, compared to an inert atmosphere.

Our lab-produced chars have characteristic low H/C ratios, small surface areas and no significant isotopic depletion on charring, typical of low temperature fires (400–500 °C). They also represent BC-rich materials formed at a lower temperature than soot, which normally forms > 500 °C and so contribute to the span of BC-rich materials that can be used as reference materials for analysis. By analysing the above characteristics for natural chars, it may become possible to estimate a burning temperature range for chars. Interestingly, the few natural chars analysed for H/C, specific surface area and $\delta^{13}C$ value, so far display characteristics of high temperature burning. It could be that (1) natural fires do not form much char, due to the presence of oxygen and the preferential formation of ash, or (2) low temperature chars actually form but transport and subsequent storage in soil and sediment selectively preserve the chemically more resistant high temperature chars.

To summarise, the lab-produced wood and grass char analysed here (1) represent typical low temperature chars, according to elemental composition H/C, $\delta^{13}C$ value and surface area and (2) can be reproduced, so they can be used as reference materials to calibrate BC methods for comparative studies.

Acknowledgements

Michael Schneider (ETH) performed the elemental analysis. The BC steering committee (M.W.I. Schmidt, C.A. Masiello, J.O. Skjemstad, D.M. Smith, L.A. Currie) initiated a project to study reference materials for black carbon analysis. We thank two anonymous reviewers for constructive comments.

Associate Editor—**Sylvie Derenne**

References

Almendros, G., Knicker, H., Gonzalez-Vila, F.J., 2003. Rearrangement of carbon and nitrogen forms in peat after progressive thermal oxidation as determined by solid-state ^{13}C- and ^{15}N-NMR spectroscopy. Organic Geochemistry 34, 1559–1568.

Baldock, J.A., Smernik, R.J., 2002. Chemical composition and bioavailability of thermally altered *Pinus resinosa* (Red pine) wood. Organic Geochemistry 33, 1093–1109.

Braadbaart, F., Boon, J.J., Veld, H., David, P., Van Bergen, P.F., 2004. Laboratory simulations of the transformation of peas as a result of heat treatment: changes of the physical and chemical properties. Journal of Archaeological Science 31, 821–833.

Brown, R.A., Kercher, A.K., Nguyen, T.H., Nagle, D.C., Ball, W.P., 2006. Production and characterization of synthetic wood chars for use as surrogates for natural sorbents. Organic Geochemistry 37, 321–333.

Czimczik, C.I., Preston, C.M., Schmidt, M.W.I., Werner, R.A., Schulze, E.-D., 2002. Effect of charring on mass, organic carbon, and stable carbon isotope composition of wood. Organic Geochemistry 33, 1207–1223.

Kim, S., Kramer, R.W., Hatcher, P.G., 2003. Graphical method for analysis of ultrahigh-resolution broadband mass spectra of natural organic matter, the Van Krevelen diagram. Analytical Chemistry 75, 5336–5344.

Krull, E.S., Skjemstad, J.O., Graetz, D., Grice, K., Dunning, W., Cook, G., Parr, J.F., 2003. ^{13}C-depleted charcoal from C_4 grasses and the role of occluded carbon in phytoliths. Organic Geochemistry 34, 1337–1352.

Kuhlbusch, T.A.J., 1998. Black carbon and the carbon cycle. Science 280, 1903–1904.

Nguyen, T.H., Brown, R.A., Ball, W.P., 2004. An evaluation of thermal resistance as a measure of black carbon content in diesel soot, wood char, and sediment. Organic Geochemistry 35, 217–234.

Preston, C.M., Trofymow, J.A., Niu, J., Fyfe, C.A., 1998. ^{13}CPMAS-NMR spectroscopy and chemical analysis of coarse woody debris in coastal forests of Vancouver Island. Forest Ecology and Management 111, 51–68.

Schmidt, M.W.I., Masiello, C.A., Skjemstad, J.O., 2003. Final recommendations for reference materials in black carbon analysis. EOS 84, 582–583.

Turney, C.S.M., Wheeler, D., Chivas, A.R., 2006. Carbon isotopic fractionation in wood during carbonization. Geochimica et Cosmochimica Acta 70, 960–964.

Zhu, D., Kwon, S., Pignatello, J.J., 2005. Adsorption of single-ring organic compounds to wood charcoals prepared under different thermochemical conditions. Environmental Science and Technology 39, 3990–3998.

Comparison of quantification methods to measure fire-derived (black/elemental) carbon in soils and sediments using reference materials from soil, water, sediment and the atmosphere

Karen Hammes [a], Michael W. I. Schmidt [a,], Ronald J. Smernik [b], Lloyd A. Currie (Ret.) [c], William P. Ball [d], Thanh. H. Nguyen [d,**], Patrick Louchouarn [e,***], Stephane Houel [e], Örjan Gustafsson [f], Marie Elmquist [f], Gerard Cornelissen [f], Jan O. Skjemstad [g], Caroline A. Masiello [h], Jianzhong Song [i], Ping'an Peng [i], Siddhartha Mitra [j], Joshua C. Dunn [j], Patrick G. Hatcher [k], William C. Hockaday [k], Dwight M. Smith [l], Christoph Hartkopf-Fröder [m], Axel Böhmer [m], Burkhard Lüer [m], Barry J. Huebert [n], Wulf Amelung [o], Sonja Brodowski [o], Lin Huang [p], Wendy Zhang [p], Philip M. Gschwend [q], D. Xanat Flores-Cervantes [q], Claude Largeau [r], Jean-Noël Rouzaud [r], Cornelia Rumpel [s], Georg Guggenberger [t], Klaus Kaiser [t], Andrei Rodionov [t], Francisco J. Gonzalez-Vila [u], José A. Gonzalez-Perez [u], José M. de la Rosa [u], David A.C. Manning [v], Elisa López-Capél [v], Luyi Ding [w]*

[a] Department of Geography, University of Zurich, Winterthurerstrasse 190, Zurich 8057, Switzerland
[b] Soil and Land Systems, School of Earth, Environmental Sciences, University of Adelaide, Waite Campus, Urrbrae SA 5064, Australia
[c] National Institute of Standards and Technology, Gaithersburg, MD 20899, USA
[d] Department of Geography and Environmental Engineering, Johns Hopkins University, USA
[e] Department of Earth and Environmental Sciences, Geoscience Bldg, Rm 110, Lamont-Doherty Earth Observatory, Columbia University, P.O. Box 1000, 61 Route 9W. Palisades, New York 10964-8000
[f] Department of Applied Environmental Science (ITM), Stockholm University, SE-106 91 Stockholm, Sweden
[g] CSIRO Land and Water, Glen Osmond, Australia
[h] Department of Earth Science, Rice University, Houston, USA
[i] State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, P.R. China
[j] Department of Geological Sciences and Environmental Studies, Binghamton University, Binghamton, New York, USA
[k] Environmental Molecular Science Institute, Ohio State University, 100 W. 18th Ave. Columbus, Ohio 43210, USA
[l] Department of Chemistry and Biochemistry, University of Denver, Denver, USA
[m] Geologischer Dienst NRW, De-Greiff-Str. 195, 47803 Krefeld, Germany
[n] Department of Oceanography, University of Hawaii, USA
[o] Institute of Crop Science and Resource Conservation, Division of Soil Science, University of Bonn, Nussallee 13, 53115 Bonn, Germany
[p] Air Quality Research Division, Atmospheric Science and Technology Directorate, Science and Technology Branch, Environment Canada, Canada
[q] R.M. Parsons Laboratory, MIT 48-413, Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

[*] Corresponding author phone: +41 44 635 5140, fax: +41 44 635 6848, e-mail: mschmidt@geo.unizh.ch
[**] Present address: Department of Civil and Environmental Engineering, University of Illinois at Urbana-Champaign, 250 N.Mathews, 3230 Newmark Lab, MC 205, Urbana IL 61801, USA
[***] Present address: Depts. of Oceanography and Marine Sciences, Texas A&M University, 5007 Avenue U, Galveston, TX 77551, USA

[r] Laboratoire de Chimie Bioorganique et Organique Physique, UMR CNRS 7618 BIOEMCO, Ecole Nationale Supérieure de Chimie de Paris, France
[s] Laboratoire Biogéochimie et écologie des milieux continentaux, Site du Centre INRA Versailles-Grignon, Bâtiment Eger, 78850 Thivernal-Grignon, France
[t] Institute for Soil Science and Plant Nutrition, Martin Luther University, Halle-Wittenberg, Germany
[u] Department Biogeoquímica y Dinámica de Contaminantes, Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS-CSIC), Av Reina Mercedes, 10- 41080, Sevilla, Spain
[v] School of Civil Engineering and Geosciences, University of Newcastle upon Tyne, Newcastle NE1 7RU, UK
[w] Analysis and Air Quality Division, Environmental Technology Center, Ontario, Canada

Abstract

Black carbon (BC), the product of incomplete combustion of fossil fuels and biomass (called elemental carbon (EC) in atmospheric sciences), was quantified in 12 different materials by 17 laboratories from different disciplines, using seven different methods. The materials were divided in three classes: (1) potentially interfering materials, (2) laboratory-produced BC-rich materials, and (3) BC-containing environmental matrices (from soil, water, sediment, atmosphere). This is the first comprehensive intercomparison of this type (multi-method, multi-lab, multi-sample), focusing mainly on methods used for soil and sediment BC studies. Results for the potentially interfering materials (which by definition contained no fire-derived organic carbon) highlighted situations where individual methods may overestimate BC concentrations. Results for the BC-rich materials (one soot and two chars) showed that some of the methods identified most of the carbon in all three materials as BC, whereas other methods identified only soot carbon as BC. The different methods also gave widely different BC contents for the environmental matrices. However, these variations could be understood in the light of the findings for the other two groups of materials, i.e. that some methods incorrectly identify non-BC carbon as BC, and that the detection efficiency of each technique varies across the BC continuum.

We found that atmospheric BC quantification methods are not ideal for soil and sediment studies as in their methodology these incorporate the definition of BC as light-absorbing material irrespective of its origin, leading to biases when applied to terrestrial and sedimentary materials. This study shows that any attempt to merge data generated via different methods must consider the different, operationally defined analytical windows of the BC continuum detected by each technique, as well as the limitations and potential biases of each technique. A major goal of this ring trial was to provide a basis on which to choose between the different BC quantification methods in soil and sediment studies. In this paper we summarize the advantages and disadvantages of each method. In future studies, we strongly recommend the evaluation of all methods analyzing for BC in soils and sediments against the set of BC reference materials analyzed here.

Keywords: black carbon, elemental carbon, intercomparison, soil, water, sediment, atmosphere

1. Introduction

The incomplete combustion of fossil fuels or biomass leads to the formation of carbon-rich (>60 %), aromatic residues (char) and condensates (soot) (Novakov, 1984; Goldberg, 1985; Akhter et al., 1985). These residues and condensates, collectively called elemental carbon (EC, used in atmospheric sciences) or black carbon (BC, used in soil and sediment sciences), seem to be ubiquitous in the atmosphere, marine sediment, soil, and water, and influence a wide range of biogeochemical processes (Schmidt and Noack, 2000; Watson et al., 2005). In this paper we will use the term black carbon (BC) to imply both BC and EC as originally defined for soil and sediments and

atmospheric studies respectively. Readers are encouraged to refer to Andreae and Gelencsér (2006) where clear definitions of EC and BC are given. A recent escalation in interest in BC can be attributed to its potential role in global warming. In fact, BC is of interest in this field for two quite different and independent reasons. First, BC has a direct effect on Earth's radiative heat balance and visibility (Crutzen and Andreae, 1990; Watson et al., 2005). Here it is the literally the "blackness" of BC that is important. Second, and for the purposes of this paper, BC in soils and sediments is defined as a carbonaceous substance of pyrogenic origin, which is resistant to thermal or chemical degradation under the conditions applied in the methods under discussion. According to estimates found in literature, >80 % of BC produced ends up in the soil, where it can reside for hundreds to thousands of years, being relatively resistant to biological and chemical breakdown (Forbes et al., 2006, Preston and Schmidt, 2006). Black carbon therefore represents a pool of C with a long residence time – in essence BC is a carbon sink. For soils and sediments, the light-absorbing characteristics of the substance are not part of our definition of black carbon. What is important is the chemical and thermal stability (and hence longevity) of BC either due to chemical recalcitrance that is evident from its aromatic structure or physical protection due to its surface functionality and binding with minerals and other organic compounds (Brodowski et al., 2005a; Forbes et al., 2006). A consequence of BC playing a different role in the atmosphere to that played in terrestrial and marine environments is that two different sets of methodologies have been developed for its quantification. In atmospheric sciences, BC is usually quantified using optical methods that rely on the light-absorbing properties of BC. In contrast, methods developed for the quantification of BC in soils and sediments rely on its resistance to degradation, and in particular, oxidation. The goal of this study is to compare how different methods, designed for soils and sediments, quantify BC in a variety of environmental materials. Therefore, we are focused on the resistance of BC to degradation, rather than to its light-absorbing and scattering properties. Several different techniques have been developed for quantification of BC in soils and sediments. Even though they all rely on the same basic principle – that BC is more resistant to breakdown than other forms of organic matter – the nature of the attacking species and the conditions of reaction vary widely. More tellingly, the BC contents determined by these different techniques also vary widely. In a recent intercomparison study of BC in soils, measured concentrations varied by up to a factor of 500 (Schmidt *et al*., 2001). In the field of atmospheric science, a large number of intercomparative studies of BC quantification have been published, as detailed in the review of Watson et al. (2005). These studies generally found smaller variations in BC contents determined by different techniques or measured in different labs. However, variation was still considerable, with differences of a factor of two common (Watson et al., 2005).

A major problem in quantifying BC is that it is not a single entity, but rather exists as a chemical continuum (Figure 1, upper part), ranging from large pieces of slightly charred biomass (1-100 μm), to sub-micron soot particles (30-40 nm) (Goldberg, 1985; Hedges *et al*., 2000; Masiello, 2004). The chemistry of these materials varies with the degree of fire exposure and the production mechanism (Kuhlbusch *et al*., 1996; Baldock and Smernik, 2002; Czimczik *et al*., 2002; Nguyen *et al*., 2004a). While char retains some plant chemistry and morphology (Sharma *et al*., 2004), soot is produced from the condensation of gas phase intermediates, and its geochemistry reflects combustion conditions and not plant or fuel precursors. During combustion, both residues (char material) and condensates (soot) can form simultaneously, and may co-exist in environmental samples (Poirier *et al*., 2000, 2002; Schmidt *et al*., 2002; Jonker and Koelmans, 2002; Fernandes *et al*., 2003; Brodowski *et al*., 2005a). Depending on the formation conditions (e.g. temperature), chars and soot can have overlapping properties, such as specific surface area and oxidative kinetics, confounding the detection of these different forms of BC. Chemical variations of BC within this combustion continuum cause methodological problems, because each BC method may be intentionally or inadvertently optimized to detect a particular form of BC. Regional or even global black carbon budgets based on measurements of different components of the black carbon continuum (remaining charred biomass, released soot) in different matrices (soil, atmosphere, water, sediments) obtained with different methods will

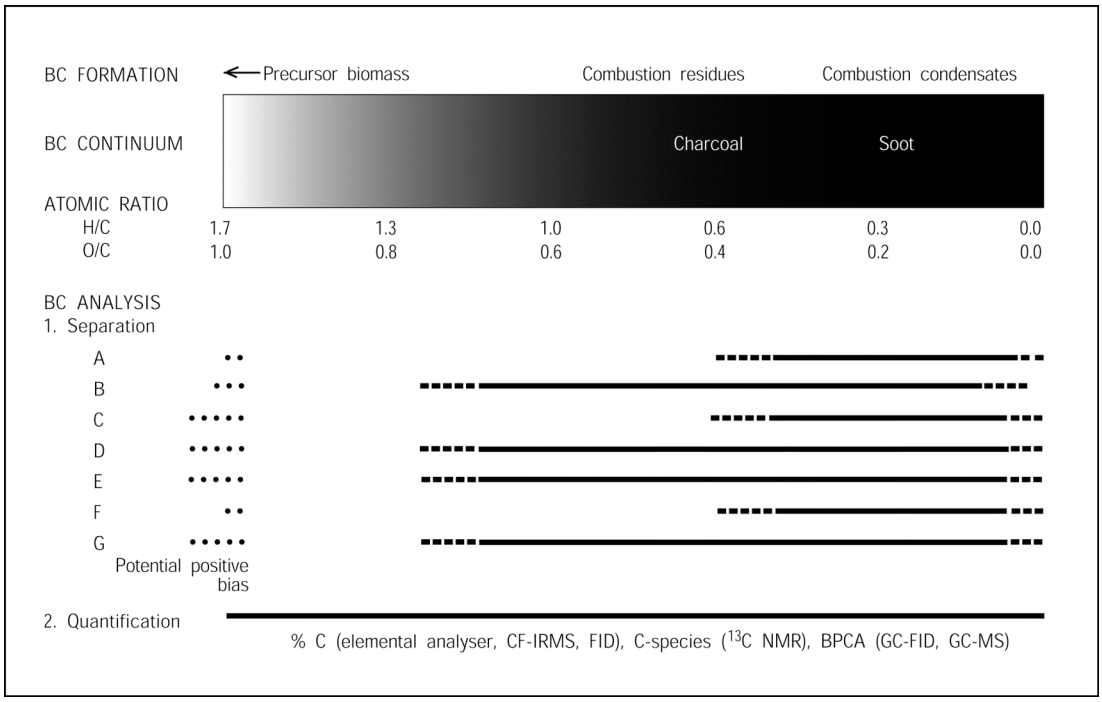

Figure 1 Conceptual summary of the comparative analyses of the seven methods to quantify black carbon (BC). The BC continuum ranges from biomass (not affected by fire) on the left to pyrogenic, highly condensed aromatic structures at the right hand side, and is plotted along a scale of atomic H/C and O/C ratios, also used in van Krevelen plots. Note that the H/C scale is non-linear. BC analysis has two steps: (1) Separation of BC was performed by seven methods: CTO-375, BPCA, Cr_2O_7, TOT/R, TG-DSC, NaClO and UV. The analytical ranges of separation are conceptual only, visualized by the use of solid and dotted lines. The dashed lines at each end of the solid lines indicate the uncertainty in the range of the BC continuum that each method measures, e.g. how much soot or partially charred biomass a certain method measures. The dots on the left of the figure indicate the potential for positive bias from the potential interfering materials for each method. (2) Quantification of BC in the operationally defined separates includes elemental analysis (to quantify carbon left after separation), ^{13}C NMR spectroscopy (to identify condensed aromatic C) or the use of gas chromatography with different detectors (GC/FID, GC/MS) to quantify the molecular markers of black carbon (BPCA). The figure was inspired by Hedges *et al.* (2000) and Masiello (2004).

likely underestimate the true loading of BC. Conversely, the biases associated with each method (charring, false-positive for refractory kerogens) will lead to an over-estimate of the true loading of BC. The need for a wide-ranging comparative study of methods used for quantification of BC in soils and sediments is clear. There has only been one other comparative study for soils (Schmidt et al., 2001). The current study is the first wide-ranging study (multi-material, multi-method, multi-lab) comparing quantification methods for soils and sediments. This study should serve as a basis for further systematic studies on these methods, to answer the myriad of questions that will surely arise from this study. A set of reference materials was selected for this intercomparison, covering a broad spectrum of environmental conditions (Schmidt et al., 2003).

These reference materials included (1) five BC-containing environmental matrices for which BC quantification is often sought, (2) three laboratory-produced BC-rich materials, and (3) four potentially interfering materials containing little or fire-derived carbon. Seventeen laboratories, using seven different analytical approaches (with variations), analyzed these samples for black carbon.

This inter-method comparison is a step in the direction of refining BC quantification methods used in soil and sediment studies in order to better compare data from different methods. Within the scope of BC quantification in soils and sediments, we address the following questions in this paper: (1) how is BC defined for each method? (2) how BC values

from different methods and laboratories compare? (3) what are potential biases for each method? and (4) what are the strengths and weaknesses of each method?

2. Experimental section

2.1. Reference materials

Twelve reference materials in three categories were used: (1) potential interfering materials (melanoidin, shale, lignite coal and bituminous coal), (2) laboratory-produced BC-rich materials (n-hexane soot, wood char and grass char), and (3) examples of environmental matrices that commonly contain BC (aerosol from an urban area, harbor marine sediment, a sand-rich soil (Chernozem), a clay-rich soil (Vertisol), and dissolved organic matter (DOM) from a river). Details on these materials can be found in Table 1.

2.2. Black carbon quantification methods

Seventeen laboratories used seven different quantification methods. The laboratories are identified in Supplement 1. The method details, including references to more specific parameters, are presented in Table 2.

2.3. Statistics

We did not use a hidden code on the samples and, therefore, trust that each laboratory was honestly reporting its analytical precision. Basic statistics were applied to the results at intra-laboratory level: standard deviation (s) and coefficient of variation (CV). Beyond that, at inter-laboratory level, we used chemo-graphical statistical tools to explore the data further, i.e. a Youden plot (Youden, 1959) and data filtering (with relative standard uncertainty, u_r).

3. Results and discussion

3.1. Comparative study set-up

Black carbon concentrations in the twelve reference materials were determined by 17 laboratories using seven distinct methods described earlier (Table 2). Three to five laboratories used methods CTO-375, BPCA, Cr_2O_7, TOT/R, whereas single laboratories used methods TG-DSC, NaClO and UV. The results of these analyses are summarized in Figure 2 (expressed as BC as proportion of OC as determined by each laboratory individually (%)) and presented in Supplement 2 (expressed as g BC kg^{-1} material), and are discussed below by first considering the results for each reference material in turn. A discussion of intra- and inter-laboratory reproducibility follows. Finally, we discuss the advantages and disadvantages of each method, and some considerations for future BC studies in soils and sediments.

3.2. Potentially interfering materials

3.2.1. Melanoidin

The melanoidin was included in the study to act as a negative control, i.e. as a sample that contains no material produced by combustion. Melanoidins have been suggested to have similar chemistry to that of natural organic matter (Benzing-Purdie and Ripmeester, 1983). It should be noted that melanoidin is not the perfect negative control sample. Any environmental matrix (e.g. soil or sediment) will contain, along with any BC, non-BC organic matter in a myriad of forms, some of which may have a similar chemistry to melanoidin, but most of which probably will not. However, there are clear practical constraints on the number of samples that can be included in an exercise such as this, and in this comparative study melanoidin was chosen to serve as a single negative control.

On average, the highest BC/OC % values were reported by laboratories using method TOT/R (44.8-65.5% BC/OC; one outlier: 18.1%). This method relies on the transmittance and reflectance of a material after oxidation, and the dark color of this material probably aided premature oxidation in the melanoidin (Currie et al., 2002). This raises some concern as to how this method discriminates between organic carbon and black carbon, since the method was developed specifically for the analysis of small quantities of aerosols collected on filters *in situ*, to study radiation effects in the atmosphere (Schauer *et al*., 2003; Chow *et al*., 2004). It would appear that this method, as it was used in the study, is not suitable for the analysis of bulk solid residues as is done in soil and sediment studies. However, resuspension of solids should be possible under certain circumstances. Other methods (CTO-375, BPCA and TG-DSC) measured about 10 times less BC/OC in the melanoidin, while methods Cr_2O_7, NaClO and UV reported BC/OC of zero percent. For method BPCA this confirms that the condensed aromatic structures forming the markers detected by this method can be present in low

Table 1 Black carbon reference materials used in ring trial with selected characteristics

Material	Selected references	Production/collection method	Organic carbon * (g kg^{-1} mass)	Surface area (g m^{-2})	Lightness (L)	Rationale
GROUP 1: Potential interfering materials						
Melanoidin	Elmquist et al., 2006	Residue formed on reaction of urea with glucose at 90 °C for 30 days	541.3 (30.1)	2.9	8.1	Negative control – contains no pyrogenic BC
Green River shale	Petsch et al., 2001 Elmquist et al., 2006	Sampled from the Mahogany zone of the Green River formation (Utah, USA)	272.5 (12.9)	0.8	44.4	Contains chemically resistant carbon but has no pyrogenic origin
Beulah-Zap lignite coal	Vorres, 1990	Sampled in Mercer County (North Dakota, USA)	589.6 (101.3)	1.6	0.4	An immature coal to differentiate coal from pyrogenic BC
Pocahontas bituminous coal	Vorres, 1990	Sampled in Buchanan County (Virginia, USA)	846.1 (62.6)	1.9	9.2	A mature coal to differentiate coal from pyrogenic BC. Can contain up to 10% inertinite in some cases.
GROUP 2: Laboratory-produced BC-rich materials						
n-hexane Soot	Akhter et al., 1985 Smith and Chughtai, 1995	Produced by open n-hexane flame and collected from the top of the flame on an inverted funnel surface	921.3 (32.9)	73.9	0.1	Represents BC produced in the gas phase (condensate) from a fossil fuel
Wood char	Elmquist et al., 2006 Hammes et al., 2006	Chestnut hardwood (*Castanea sativa*) char was produced at 450 °C for 5 hours (holding time) in inert N atmosphere (Tessin, Switzerland)	744.4 (45.6)	2.0	6.0	Represents BC produced in the solid phase (residue) from wood material (biomass)
Grass char	Elmquist et al., 2006 Hammes et al., 2006	Grass char (*Oryza sativa*) was produced at 450 °C for 5 hours (holding time) in inert N atmosphere (Tessin, Switzerland)	591.4 (32.0)	5.9	5.7	Represents BC produced in the solid phase (residue) from grass material (biomass)
GROUP 3: Environmental matrices						
Urban dust (SRM 1649a)	Currie et al., 2002 Masiello et al., 2002 NIST, 2001	Sampled in 1976-1977 as atmospheric particulate matter from the Washington DC area (USA)	178.4 (6.3)[b]	3.7	15.4	Represents BC[c] soot in a aerosol matrix
Marine sediment (SRM 1941b)	Elmquist et al., 2006 NIST, 2004	Sampled from the Baltimore Harbor in the Chesapeake Bay area (USA)	30.7 (4.0)[b]	28.6	53.5	Represents BC soot in a sediment matrix
Vertisol	Schmidt et al., 2001	Sandy clay soil sampled at a 0-10 cm depth at Urrbrae (South Australia), 37% clay	31.3 (2.3)	57.3	30.7	Represents BC char in a soil matrix with a high clay content
Chernozem	Schmidt et al., 2001	Light sandy clay soil sampled at a 20–60 cm depth in the Hildesheim-Braunschweig region (Harsum, Germany), 19% clay	19.3 (0.9)	9.0	32.0	Represents BC char in a soil matrix with a low clay content
Dissolved organic matter (DOM)	Serkiz and Perdue, 1990 Elmquist et al., 2006	Collected from the Suwannee River using reverse osmosis (Georgia, USA)	459.4 (37.6)	-	25.9	Could contain soluble condensed aromatic structures

[a] Organic carbon content for each material averaged over all the laboratories (standard deviation in brackets)
[b] Organic carbon for TOT/R methods is total carbon minus black carbon
[c] called EC in atmospheric sciences (see Currie et al., 2002)

Table 2 Methods employed in ring trial and individual modifications

Method A: Chemo-thermal oxidation at 375 °C (CTO-375). In this method samples are pretreated with acid to remove carbonates and then thermally oxidized to eliminate labile carbon and leave a resistant residue for quantification as BC.

Lab	Selected references	Pretreatment		Oxidation				Detection
		Acid	Mode	Time	Initial oven temp	Temperature ramp	Atmosphere	
1	Gustafsson et al., 1997 Nguyen et al., 2004	1 HCl	Crucible (except soot and chars)	24 h	360 °C	2.5 °C min^{-1} to 375 °C		Elemental analysis on residue Mass difference between before oxidation and after
5	Gustafsson et al., 1997	0.7 M H_2SO_3	Ag capsule	24 h	*23 °C	60 °C min^{-1} to 360 °C 30 °C min^{-1} to 370 °C 3 °C min^{-1} to 375 °C		Elemental analysis on residue Mass difference between before oxidation and after
7a	Gustafsson et al., 1997 Gustafsson et al., 2001	1 M HCl 20 min grinding with automatic ball grinder	Ag capsule	18 h	*23 °C	10 °C min^{-1} to 350 °C 0.5 °C min^{-1} to 375 °C		[b]CF-IRMS, followed by coulometric quantification of CO_2
7b	Gustafsson et al., 1997 Gustafsson et al., 2001 Elmquist et al., 2004	Standard addition of incremental amounts of standard reference material SRM 2975 to marine sediment and urban dust. Rest of procedure as for 7a.						
12a	Gustafsson et al., 1997 Gustafsson et al., 2001 Gélinas et al., 2001	32 % HCl 10 % HF/1 M HCL wash	Crucible - vapor	18 h	*23 °C	11 °C min^{-1} to 375 °C		CF-IRMS, followed by coulometric quantification of CO_2
12b	Gustafsson et al., 1997 Gustafsson et al., 2001	32 % HCl	Crucible - vapor	18 h	*23 °C	11 °C min^{-1} to 375 °C		CF-IRMS, followed by coulometric quantification of CO_2

[a] Crucible acidification made *ex situ*, Ag capsule acidification made *in situ*

[b] CF-IRMS – Continuous Flow Isotope Ratio Mass Spectrometer

* assumed room temperature

Table 2 Methods employed in ring trial and individual modifications (continued)

Method B: Benzene polycarboxylic acids (BPCA). In this method samples are pretreated to remove metals and carbonates. The samples are then oxidized to isolate aromatic structures that are converted into benzene polycarboxylic acids. Black carbon is quantified as the sum of the three- to six fold carboxylated benzoic acids that are measured using gas chromatography and flame ionization detection (GC/FID). Black carbon yields were multiplied by a conversion factor of 2.27 to estimate BC quantities.

Lab	Selected references	Pretreatment			Oxidation			Detection	
		Time	Temperature	Acid	Time	Temperature	Acid	Instrument	Temperature program
2	Glaser et al., 1998 Brodowski et al., 2005b	4 h	105 °C	4 M TFA	8 h	170 °C	65 % HNO_3	GC-FID 30 m x 0.32 mm i.d., 0.25 µm film	100 °C held for 2 min 20 °C min^{-1} to 240 °C held for 7 min 30 °C min^{-1} to 300 °C held for 10 min
6	Glaser et al., 1998 Brodowski et al., 2005b	4 h	105 °C	4 M TFA	8 h	170 °C	65 % HNO_3	GC-FID 30 m x 0.25 mm i.d., 0.25 µm film	100 °C held for 2 min 20 °C min^{-1} to 240 °C held for 7 min 30 °C min^{-1} to 300 °C held for 10 min
14	Glaser et al., 1998 Brodowski et al., 2005b	4 h	105 °C	4 M TFA	8 h	170 °C	65 % HNO_3	GC-MS 50 m x 0.2 mm i.d., 0.33 µm film	70 °C held for 2 min 15 °C min^{-1} to 200 °C held for 5 min 5 °C min^{-1} to 300 °C held for 15 min

Table 2 Methods employed in ring trial and individual modifications (continued)

Method C: Acid dichromate oxidation (Cr_2O_7). Samples are pretreated to remove carbonates. Black carbon is defined as the organic carbon that survives oxidation with dichromate. Oxidation of carbon in the residue is modeled as first order exponential loss process, with a "fast" component (ca. six hours) corresponding to labile, non-BC oxidation, an intermediate component corresponding to kerogen, and a "slow" component (100-1000 hours) corresponding to BC.

Lab	Selected references	Pretreatment			Oxidation			Detection
		Time	Temperature	Acid	Time	Temperature	Acid	
11	Bird & Gröcke, 1997 Rumpel et al., 2006			10 % HF	24 h	80 °C	0.1 M $K_2Cr_2O_7$/ 2 M H_2SO_4	Elemental analysis Mass difference between before and after oxidation
13	Wolbach & Anders, 1989	24 h	22.5±2 °C	6 M HCl/53 % HF	400 h	22.5±2 °C	0.25 M $K_2Cr_2O_7$/ 2 M H_2SO_4	Elemental analysis Mass difference between before and after oxidation
16b	Lim & Cachier, 1996 Song et al., 2002	20 h	60 °C	6 M HCl	10 min	*23 °C in ultrasonic bath	0.1 M $K_2Cr_2O_7$/ 2 M H_2SO_4	Elemental analysis Mass difference between before and after oxidation
		20 h	60 °C	6 M HCl/22 M HF	60 h	55 °C in water bath		
		10 h	60 °C	6 M HCl				
17	Lim & Cachier, 1996	15 min	*23 °C in ultrasonic bath	3 M HCl	15 min	*23 °C in ultrasonic bath	0.5 M $K_2Cr_2O_7$/ 2 M H_2SO_4	Elemental analysis Mass difference between before and after oxidation
		24 h	*23 °C					
		15 min	*23 °C in ultrasonic bath	10 M HF/1 M HCl	48 h	55 °C		
		24 h	*23 °C					

*assumed room temperature

Table 2 Methods employed in ring trial and individual modifications (continued)
Method D: Thermal/optical transmittance and reflectance (TOT/R). BC is defined as the integrated part after the split point where the laser transmittance or reflectance equals the initial laser value.

Lab	Selected references	Pretreatment	Oxidation						Detection
			First heating step		Second heating step		Third heating step		
			Temperature	Atmosphere	Temperature	Atmosphere	Temperature	Atmosphere	
3	Chow et al., 1993	No	*23 °C to 550 °C	He	Up to 800 °C under	2 % O_2/He			He-Ne laser reflectance (632 nm) plus FID
9a	Huang et al., 2006	No	*23 °C to 550 °C	He	Up to 870 °C	He	Up to 900 °C	10 % O_2/ 90 % He	Integrated fraction of plateau at 900 °C plus FID
9b	Chow et al., 1993 Huang et al., 2006	No	*23 °C to 550 °C	He	Up to 870 °C	He	Up to 900 °C	10 % O_2/ 90 % He	He-Ne laser transmittance (632 nm) plus FID
10	Chow et al., 1993 Schauer et al., 2003 Huebert et al., 2004	No	From 250 °C to 870 °C	He	Cooling to 550 °C	He	Up to 900 °C	10 % O_2/ 90 % He	He-Ne laser transmittance (632 nm) plus FID
16a	Chow et al., 1993 Cheng et al., 2005	HCl vapor	From 310 °C to 840 °C	He	Cooling and then heat to 550 °C	He	Up to 860 °C	10 % O_2/ 90 % He	He-Ne laser transmittance (632 nm)

*assumed room temperature

Table 2 Methods employed in ring trial and individual modifications (continued)

Method E: Thermogravimetry and differential scanning calorimetry analysis (TG-DSC). This method measured carbonaceous species being thermally oxidized while recording mass loss. Initial weight loss is due to exothermic decomposition of labile aliphatic and carboxylic groups (ca. 300 °C), while exothermic loss of more refractory aromatic carbon occurs at higher temperatures (ca. 450 °C). The positions of the DSC peaks reflect the structure and chemical composition of the material.

Lab	Selected references	Pretreatment	Oxidation		Detection
			Temperature	Atmosphere	
4	Dell'Abate et al., 2000, Dell'Abate et al., 2003 Plante et al., 2003 Lopez-Capel et al., 2005	No	20 °C to 990 °C (20 °C min^{-1})	20 % O_2/80 % He	Mass difference during heating, over specific intervals that correspond to decomposition if individual components of the sample.

Method F: Sodium hypochlorite oxidation (NaClO). Samples are oxidized in NaClO to remove components that overlap with the signal of BC, such as lignin and other non-BC aromatic compounds. This is followed by organic carbon and ^{13}C nuclear magnetic resonance (NMR) analyses of the residue to determine BC from the relative amount of aromatic carbon (110-140 ppm in solid-state ^{13}C NMR).

Lab	Selected references	Pretreatment		Oxidation (repeat three times)			Detection
		Time	Acid	Time	Temperature	Acid	
8	Simpson & Hatcher, 2004a Simpson & Hatcher, 2004b	12 h	6 M HCl	4 h	*23 °C	NaClO	^{13}C NMR, Elemental analysis Mass difference between before and after oxidation

*assumed room temperature

Method G: UV photo-oxidation (UV). This method relies on the relative stability of char to high energy UV-oxidation compared to other soil organic carbon fractions.

Lab	Selected references	Pretreatment		Oxidation				Detection
		Time	Acid	Time	Temperature	Agent	Wash	
15	Skjemstad et al., 1996 Skjemstad et al., 1999		Wet sieved < 53 μm 2 % HF	2 h	*23 °C	UV photo-oxidation at 2.5 kW in oxygen saturated water	$Al_2(SO_4)_3$ and water	^{13}C NMR, Elemental analysis Mass difference between before and after oxidation

concentrations in non-pyrogenic material, such as melanoidin (Brodowski *et al*., 2005b). However, it should be noted that these markers were found at 30-50 times higher concentrations in the char and soot samples (Figure 2, Supplement 2). For method CTO-375, charring of the melanoidin during heating would seem the most likely cause of non-zero BC values determined by this method (Gustafsson *et al*., 2001).

3.2.2. Shale

The shale was included in the study because it contains chemically resistant OC that has low aromaticity (Trewhella *et al*., 1986). The OC (kerogen) in this shale is derived mainly from the alkyl biopolymers that constitute the cell walls of certain species of algae. The kerogen has undergone little thermal change and so retains its aliphatic character. Nonetheless, it does contain some aromatic C, at least some of which is in fused aromatic structures (Trewhella *et al*., 1986).

The highest BC concentration for the shale was reported by method TG-DSC (62.6%), and the second highest by method Cr_2O_7 (average BC/OC 23.3%). These methods potentially overestimate BC, since they quantify chemically recalcitrant carbon, irrespective of the nature of the carbon, and TG-DSC also reports weight losses from dehydration of clay minerals in samples of this type. Most other laboratories reported BC/OC <10% (apart from one extreme value for one laboratory from method CTO-375 and one high value for one laboratory from method TOT/R) (Figure 2).

3.2.3. Coal

The coals were included in the study to determine whether the BC quantification techniques would identify coal as BC. Coal is naturally present in a minority of soils and sediments, but is an abundant contaminant in many industrialized environments. In such environments it may be important to be able to differentiate coal from pyrogenic BC. Since coal chemistry varies greatly, two coals were chosen at either end of the maturity scale, a lignite coal (immature) and a bituminous coal (mature). The bituminous coal may contain about 10 % inertinite from ancient fire occurrences (Vorres, 1990).

The bituminous coal was found to have a higher BC content than the lignite coal for every technique. The highest BC/OC % for lignite coal was reported by method TOT/R (50.2%), followed by method UV (26.9%) and one laboratory of the BPCA method (23.4%). Most other methods reported values <20%, while methods CTO-375 and NaClO reported ≤5%. For the bituminous coal, laboratories using methods TOT/R, TG-DSC, Cr_2O_7 and UV all reported BC/OC of >70% (Figure 2); i.e., most of carbon in this sample was found to be BC using these methods. The bituminous coal was not analyzed using method NaClO. Method BPCA reported 15.8-25.9% BC/OC for the bituminous coal, indicating that it only partly consists of highly condensed material. Laboratories using method CTO-375 reported the lowest BC concentrations in both coals. In fact, the BC concentrations determined using method CTO-375 were generally at least an order of magnitude lower than those measured by other techniques.

In summary, all methods except CTO-375 and NaClO measured more than 10% BC/OC for one or more of the potential interfering materials. These materials have properties shared by BC-rich materials, like high C-content or dark color, but do not have pyrogenic origins. These potential biases should be kept in mind when analyzing environmental matrices like soils and sediments where such contaminants could be present, since it could lead to an overestimation of the BC content of the material (Chow et al., 2004).

3.3. Laboratory-produced BC-rich materials

Three materials were produced as BC-rich standards for this comparative study. These were designed to cover a range of the BC continuum, and included soot (produced in the gas phase from an inefficiently combusting hexane flame) and two chars (solid residues of combustion of solid materials under oxygen-free conditions). The two chars were produced from wood and grass residues to test whether chars produced from different starting materials are detected differently by the various BC quantification methods.

Method CTO-375 clearly differentiated between the soot and the chars – laboratories using this method reported zero BC/OC in the wood char, no more than 1.5% BC/OC in the grass char and around 48.5% BC/OC in the soot (one outlier in method CTO-375: 36.6 %; Figure 2). Similar results were reported for method NaClO – a value of zero was found for the wood char, 10.4% for the grass char, and 67.0% for the soot (Figure 2). In both methods where zero values were found, there was no

residue left to measure. The CTO-375 and NaClO methods both quantified more BC in the grass char than the wood char, which is the opposite of the other five methods. There could be specific structural properties of the grass char that resulted in it partially surviving the oxidation at 375 °C and NaClO oxidation. For example, grasses typically contain organic carbon trapped within silica phytoliths and this carbon is protected from to oxidation under these conditions. Of the other methods, laboratories using method BPCA reported the lowest BC concentrations for the soot and chars (around 26%), although these varied quite widely (by up to a factor of three) between the different laboratories that used this method (Figure 2). The other methods (Cr_2O_7, TOT/R, TG-DSC and UV) reported large concentrations of BC in all three of these materials, although the values varied by up to a factor of two (Supplement 2).

In summary, methods CTO-375 and NaClO were able to differentiate between the soot (which gave high BC values) and the chars (which gave zero and low BC values). Method BPCA gave intermediate values for BC content, whereas methods Cr_2O_7, TG-DSC and UV gave high values for BC content for all of these materials, based on the high thermal and chemical resistance of these materials (Lim and Cachier, 1996; Skjemstad et al., 1999, Lopez-Capel et al., 2005). It is possible that the dark color of these materials created problems for the TOT/R method in that the split between OC and BC became hard to discern (Chow et al., 2004).

3.4. Environmental matrices

As has been found previously (Schmidt *et al*., 2001), the BC contents reported by each of the laboratories in this study for the five environmental samples varied widely. However, by knowing how the different methods detected BC in the potentially interfering and BC-rich materials discussed above, we can draw some conclusions from these variations.

3.4.1. Aerosol

The highest BC/OC % was reported for method TG-DSC (58.9%). Method TG-DSC can overestimate BC concentrations in samples that contain clays or carbonates, which lose water or CO_2 during heating (Lopez-Capel *et al*., 2005). Methods Cr_2O_7 and TOT/R reported BC/OC ranging from about 16-50%. Laboratories using methods CTO-375 and BPCA reported similar BC/OC % (3.7-14.3%) in a lower range than the other methods, although a wider range of values was reported using method CTO-375 than method BPCA (Figure 2). The aerosol was not analyzed using method NaClO. This aerosol was first studied in detail by Currie et al. (2002), where 19 different chemical and thermal methods, including CTO-375, TOT/R, reported 6.9-52.0% EC/TC (BC/OC). This gave the first evidence that comparative results are likely to be method and matrix-dependent (Currie et al., 2002).

The relatively high BC concentration detected using method CTO-375 (8.6%) indicates a high soot content for this sample (Currie et al., 2002). This soot may have been under-detected using method BPCA, as this method recorded relatively low BC concentrations for the most condensed aromatic structures (soot, char and bituminous coal). On the other hand, method BPCA also detects small units of condensed aromatic systems. Therefore, a likely explanation for the similar BC contents reported using methods CTO-375 and BPCA would be that the aerosol contains a mixture of large and small units of condensed aromatic structures, the former of which is detected more efficiently by method CTO-375, the latter by method BPCA. Such an explanation also would be consistent with the higher BC contents recorded using methods Cr_2O_7 and UV, since these two methods detected a wide range of aromatic structures as BC in the BC-rich materials (both soot and char BC).

3.4.2. Marine sediment

The highest BC/OC % for the marine sediment was reported by method TG-DSC (100%), an unlikely value attributed to the interference of mineral impurities in the sediment (Manning et al., 2005). The lowest BC/OC % for the marine sediment were reported by laboratories using method BPCA (2.0-8.6%). Laboratories using method CTO-375 reported BC/OC in the range 12.8-22.6%. Method TOT/R showed large variation in the results (9.9-48.7%). Three of the four laboratories using method Cr_2O_7 reported BC/OC in the range 11.3-39%, and 49.4% for the UV method.

That BC concentrations were higher for method CTO-375 than method BPCA may indicate that BC in this sample is predominantly highly condensed (soot-like). However, the higher BC concentrations reported using

methods Cr_2O_7, TG-DSC and UV indicate the presence of additional BC with less condensed structures. These methods also measured high values for the shale and coals, thus also suggesting that methods Cr_2O_7, TG-DSC and UV overestimated the BC in the marine sediment.

3.4.3. Soils

The lowest BC/OC for the two soils were reported by the laboratories using method CTO-375, ranging between 1.2 and 8.7% (Figure 2). Higher BC/OC in the range 3.5-35.5% were generally reported for laboratories using methods BPCA, Cr_2O_7, TOT/R and NaClO, although there were some lower values reported using method Cr_2O_7 (Figure 2). Method Cr_2O_7 produced a wide range of values, especially for the Vertisol (3.5-19.4%) but also for the Chernozem (3.8-11.7%). The highest BC concentrations in the soils were reported by methods TOT/R, TG-DSC and UV (Figure 2). Due to the inefficient removal of interfering matrices (clays, carbonates, paramagnetics), it could be that these methods may have overestimated the BC in the soils (Currie et al., 2002, Plante et al., 2005). The random and systematic differences between the methods for these soils are further discussed under point 3.7 (Systematic evaluation of variability).

The lower BC concentrations reported using method CTO-375 for the soils as compared to the aerosol and marine sediment are consistent with differences in the source of the BC in these materials. Both the aerosol and the marine sediment were collected in highly industrialized environments in which fossil fuel burning is a major source of BC. On the other hand, the soils were collected from agricultural sites where vegetation burning is the major BC source. As discussed above, method CTO-375 specifically detects the most condensed BC and this is more prevalent in BC produced by fossil fuel burning than vegetation burning.

3.4.4. Dissolved organic matter

BC-derived material has been identified as part of the dissolved organic matter fraction in river water (e.g. Hockaday 2006). Methods Cr_2O_7 and UV were bound to find zero BC contents for DOM as each of these techniques identifies BC as an insoluble, solid residue. Laboratories using method CTO-375 also generally reported zero or near-zero BC contents for the DOM (Figure 2). This seems plausible, as this technique only identifies the most highly condensed aromatic structures (e.g. soot) as BC, and such structures are unlikely to be water-soluble. Methods TG-DSC and NaClO did not analyze the DOM. Method TOT/R reported the highest content for this material (average 33.9%) but with large variation (0-62%). Method BPCA gave two extreme values for the DOM (0.6% and 8.3%, Figure 2). It is certainly conceivable that the DOM does contain condensed aromatic structures, and that these are pyrogenically formed. Such soluble condensed aromatic structures would owe their water solubility to the presence of polar substitutions (e.g. carboxyl groups) and small molecular size (Hockaday et al., 2006).

In summary, for the environmental materials, methods TOT/R and TG-DSC are influenced by interfering matrices like carbonates and clays, in the former case because the method has been developed for samples with little or no inorganic matrix, and in the latter because clay minerals potentially decompose at similar temperatures to BC, thus giving interfering weight losses that cannot be discriminated (Manning et al., 2005.

3.5. Intra-laboratory reproducibility

Most laboratories made replicate BC measurements for each of the reference materials, which enable intra-laboratory reproducibility to be gauged. The results of these replicate measurements are shown in Supplement 2 in terms of coefficients of variance (CV) in the replicate measurements, expressed as a proportion (%) of the mean BC concentration reported by that laboratory. The mean CV increased in the order: Method TOT/R (5.1%) < CTO-375 (11.9%) < Cr_2O_7 (14.9 %) < BPCA (17.0%) < NaClO (19.4%). For the latter (method NaClO) only data for seven of the twelve reference materials were reported. The order was different when considering the range of CV, which increased in the following order: method TOT/R (0-20.3%) < NaClO (2.5-30.6%) < BPCA (0-42.9%) < CTO-375 (0-57.1%) < Cr_2O_7 (0-91.1%). The largest CV value (91.1 %) originated from duplicate analysis of the marine sediment with low absolute BC concentrations (3.7 g BC kg^{-1} dry matter) and large standard deviation (± 3.4 g BC kg^{-1}). Methods TG-DSC and UV were not replicated, and thus we could not assess reproducibility. However, for method TG-DSC, three to five replicates typically yield CV of less than 10%, and for method UV, laboratory 15 pooled four sub samples per

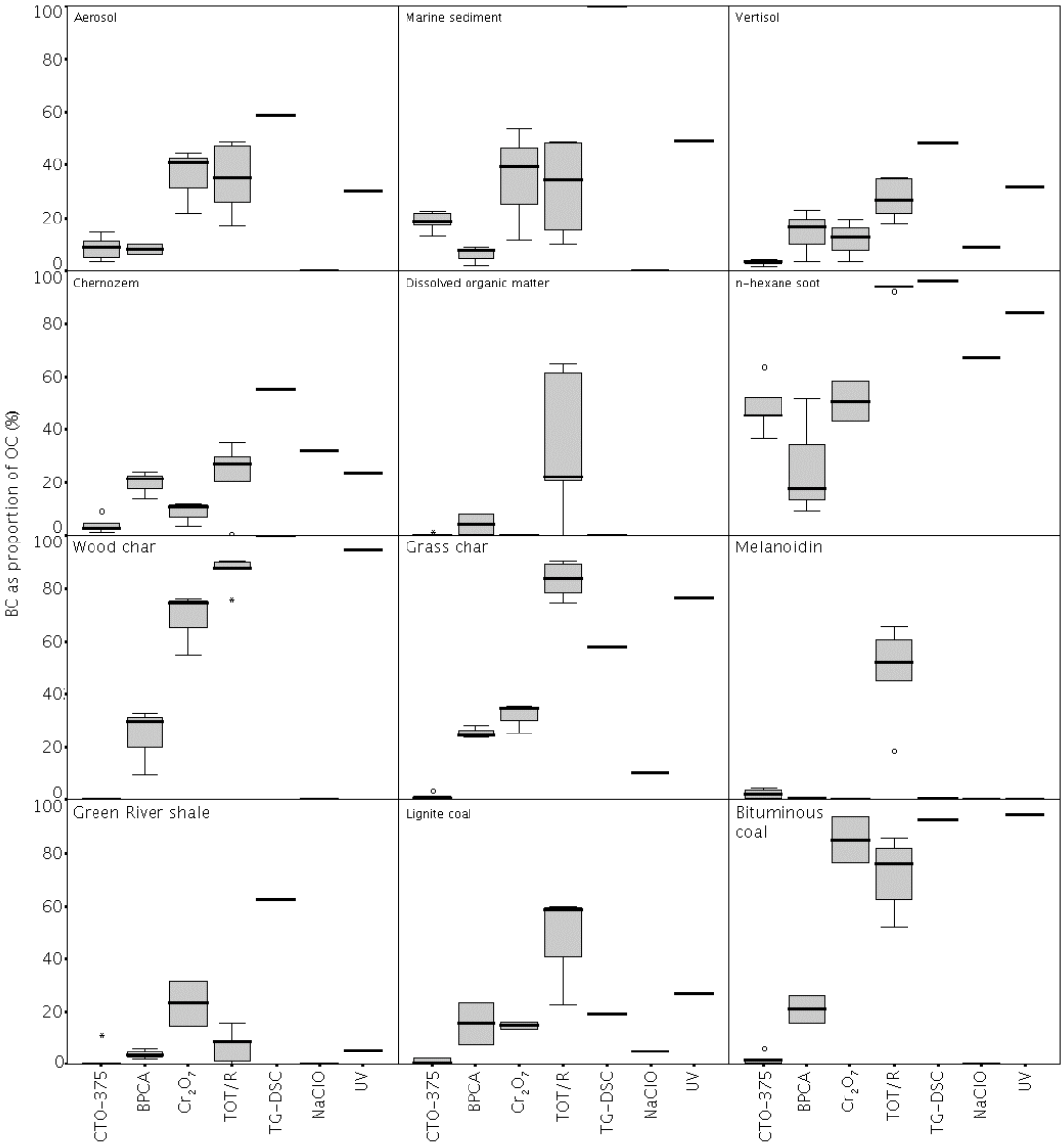

Figure 2 Black carbon concentrations for each BC reference material quantified by seven different methods. The top line of each grey bar is the highest value measured, the bottom line is the lowest value measured and the black line inside each bar is the average BC concentration for each method. For method CTO-375, N = 6; BPCA, N = 3; Cr_2O_7, N = 4; TOT/R, N = 5; TG-DSC, N = 1; NaClO, N = 1; UV, N = 1.

reference material for the final quantification step on one sample using NMR.

3.6. Inter-laboratory reproducibility (within methods CTO-375, BPCA, Cr_2O_7, TOT/R)

Variations in BC contents reported by laboratories using the same method (for methods CTO-375, BPCA, Cr_2O_7, TOT/R) were generally greater than the intra-laboratory variation discussed above. The most likely reason for this is that there were some variations in the exact methodology used (Table 2).

3.6.1. Method CTO-375

Six data sets were generated by four laboratories, which used different pretreatment and oxidation conditions. The pretreatment removes organic matter, carbonates and silicate minerals before thermal combustion takes place, that can otherwise be charred and lead to BC overestimation. The original method uses a 24-hour oxidation time, but it has been shown for some low-condensed chars the char carbon is fully removed after 18 hours (Nguyen et al., 2004). The systematic differences found between the laboratories are further discussed under point 3.7 (Statistical evaluation of variability).

3.6.2. Method BPCA

The three laboratories performing this method used essentially the same pretreatment and oxidation conditions. Actions that could influence results include: (1) aterial could be lost from the filter papers after the pretreatment wash (worse for fine BC-rich materials than environmental matrices). (2) care has to be taken not to exceed an aliquot volume of 2 mL (sample in HNO_3), to avoid the deterioration of the citric acid internal standard (Brodowski *et al.* 2005b). Nevertheless, an incomplete recovery of the internal standard at least offers a method-inherent control of accuracy, (3) slightly differing derivatization conditions (duration, temperature, standing time after derivatization), (4) column specifications and temperature program of the gas chromatograph, and (5) the type of calibration curve set up (one-point calibration vs. calibration curve).

3.6.3. Method Cr_2O_7

Four laboratories used this method, with pretreatment and oxidation conditions varying widely. Since this method quantifies the resistant carbon residue after a specific time of Cr_2O_7 oxidation, the different oxidation conditions led to substantial differences in results among laboratories.

3.6.4. Method TOT/R

Four laboratories generated five data sets using this method. Differences in sample weight as well as pretreatment and heating conditions led to substantially different results among laboratories. Laboratories using this method had difficulty spreading the material homogenously on the filter paper, leading to uneven oxidation sites and sometimes an unreliable split between OC and BC.

3.7. Statistical evaluation of variability

We used two chemo-graphical tools to identify patterns across laboratories and classes of methods. This approach could serve as a first step to aid in the process of asking qualitative and quantitative questions about underlying (artifactual, scientific) causes of the patterns.

First, we tried to reveal outliers as well as random and systematic differences within and between laboratories by using a correlation (Youden) plot (Figure 3). This graphical data analysis technique visualizes variability within a laboratory as well as variability between laboratories.

Basically, cross-plotting data from sample 1 (x-axis) and sample 2 (y-axis) helps to reveal if all laboratories behave the same. Plotting the data for the two soils (Vertisol, Chernozem, Figure 3) for all the methods, systematic differences are seen between laboratories, spanning about two orders of magnitude along the diagonal line (log scale on both axes). Outliers are indicated by deviations from the pattern or the diagonal, respectively.

Several key observations became clear: (a) All method CTO-375 results fall substantially below those of the other methods, (b) The systematic errors occur between and within methods, suggesting that subtle intra-method details may be responsible for significant differences, and (c) outlying results of laboratory 17 (method Cr_2O_7) and laboratory 9b (method TOT/R) could not be explained at first sight. Possible reasons for the observed differences between laboratories using nominally the same method are the modification in oxidation time (method CTO-375 and Cr_2O_7), and the use of an internal standard (method BPCA), which is very sensitive to chemical degradation.

Second, to reveal systematic differences within one method we selected the results from method CTO-375 as example, since it had the most data points to use (Figure 4). The data were filtered to exclude results where less than three laboratories reported data, and relative standard uncertainty (u_r) was larger than 10. The filtering elucidated ordered, and even semi-quantitative patterns (systematic differences) among all BC reference materials, except the soot and wood char, where the results were indistinguishable. For all the environmental samples, laboratory 5 always exceeded laboratory 7a (except for DOM), while the potential interfering materials showed exactly the opposite trend (except for shale). Compatible data (overlapping numbers) were obtained for marine sediment, soot, and wood char, but not for the other materials. This method was developed for measuring soot in marine sediments. The differing results for the reference materials are probably due to differences in acid pretreatment procedures and thermal oxidation time as explained above. The other methods did not reveal such systematic differences, due to either random differences or lack of data points after data filtering.

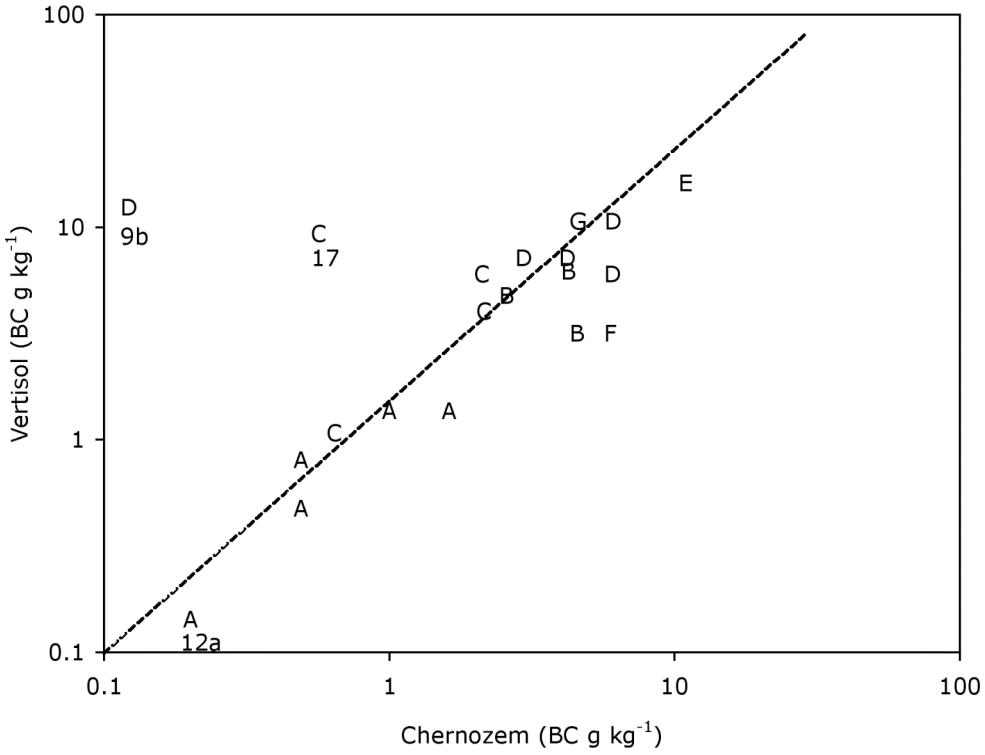

Figure 3 Correlation (Youden) plot of Vertisol (y-axis) vs. Chernozem (x-axis), showing broad systematic differences, and major discrepancies (Laboratories 9b, 17). The letters A to G correspond to the seven classes of methods and the numbers identify laboratories. The best-fit line is seen as a diagonal trend line along which most of the data lie.

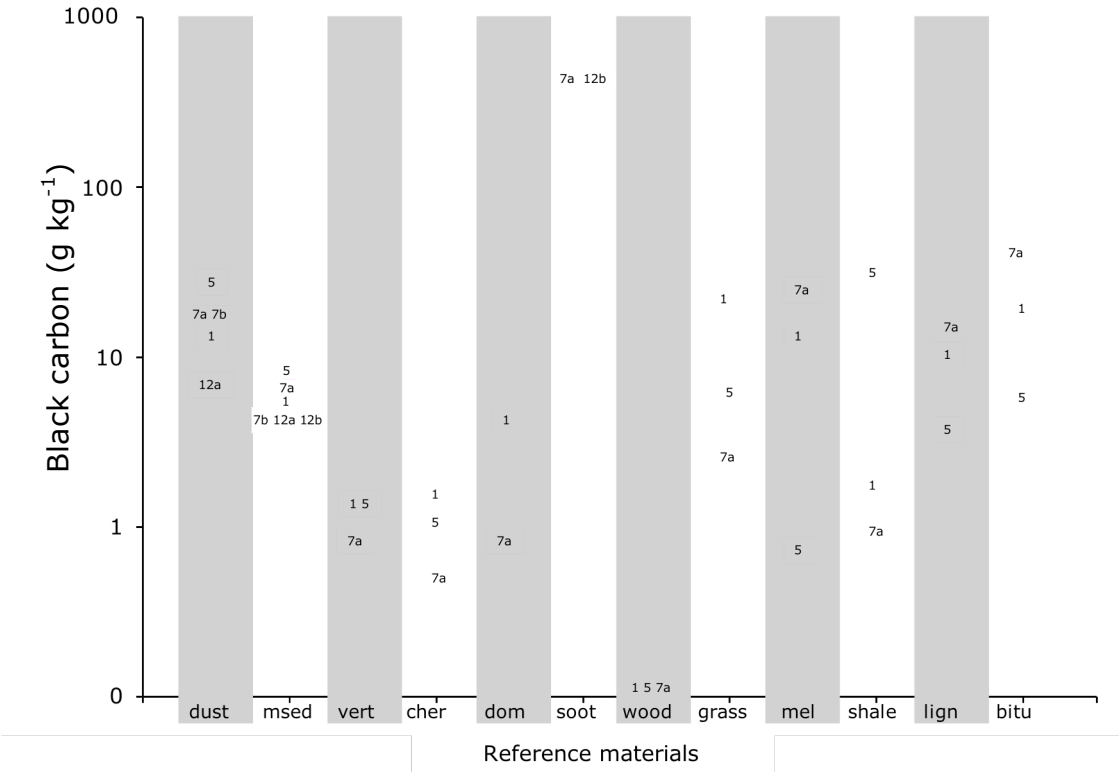

Figure 4 Log plot of CTO-375 data (y-axis) vs. reference materials (x-axis) using selected data (n>2, u_r<10 %). dust = Aerosol, msed = Marine sediment, vert = Vertisol, cher = Chernozem, dom = Dissolved organic matter, soot = n-hexane soot, wood = Wood char, grass = Grass char, mel = Melanoidin, shale = Green river shale, lign = Lignite coal, bitu = Bituminous coal. A zero code (0.11 g kg^{-1}) was used for zero values on the log plot.

3.8. Choosing between methods

The seven BC quantification methods described here are very different: they rely on a range of different properties (color, thermal and chemical stability) to differentiate BC from co-existing non-BC components and were originally developed for specific types of sample (e.g. soil, sediment, aerosol) or to quantify a specific type or range of BC (e.g. soot or char or both). The methods are also at different stages of method development – some have been used widely (though usually only for a limited range of sample types), whereas others are more recent and have only been used by a few laboratories, or perhaps only by the person/laboratory that developed them. The methods also vary in their ease of use and cost. All of these factors will come into play when choosing a BC quantification technique for a given application. A major goal of this exercise was to provide assistance in making this choice for BC quantification in soil and sediment studies. Below we summarize what we see as the advantages and disadvantages of each method, based mainly on the results of the comparative study.

3.8.1. Method CTO-375

Advantages: This method provided excellent differentiation between the soot and chars analyzed in this study and so is best suited for quantifying the most condensed forms of BC, irrespective of its source. It also did not identify coal as BC. It should be noted that while the BC concentrations determined using method CTO-375 were very low for the chars analyzed in this study (which were produced at 450°C), Nguyen *et al*. (2004a) found that chars produced at higher temperatures (e.g. 1000 °C) partially survived the CTO-375 method. The lower formation temperature of the chars in this study allowed for more cellulose and lignin to be preserved in the material, inducing a premature oxidation of BC. The same phenomenon was found when forklift diesel soot was combined with apple leaves to make a hybrid RM. The presence of the biopolymer component led to a premature oxidation of a major part of the soot (Currie and Kessler, 2005). Most soot survives primarily because of the combination of largely graphitic outer surfaces, natural aggregation into larger particles, and perhaps a relative lack of oxygen access to internal locations, compared to chars, which are organized in smaller, less condensed units. Lowering the oxidation temperature would include recalcitrant non-pyrogenic OM as artifact, leading to an overestimation of BC.

A higher BC content has been reported for diesel soot using this method (Gustafsson *et al*., 1997; 2001; Elmquist *et al*., 2004, 2006). The relative degree of thermal oxidative stability was explicitly and quantitatively demonstrated in Elmquist et al (2006) to be wood-char < grass-char < hexane-soot < diesel-soot.

Disadvantages: Since this method only quantifies highly condensed BC, it cannot give a representative view of the whole BC continuum like some gentler oxidation methods can, i.e. if low condensed char BC is present, it will not be detected. Also, gentler oxidation methods reported higher soot BC concentrations than the CTO-375 method, which is related to the relative degree of thermal oxidative stability as discussed above. As for all BC methods tested, a central challenge also for method CTO-375 is to avoid significant positive biases (e.g. charring). While this method returned the lowest interference potential for 3 out of the 4 potentially interfering materials, results for melanoidin (average 2.4% BC/OC) indicate the risk for positive bias. Such interference potential should be compared with the fraction of carbon remaining for BC material (e.g., 700 g kg^{-1} TOC for diesel soot-BC; Elmquist *et al*., 2006) and the expected relative abundances of the interfering and target substances in the studied environmental matrix. Laboratory 12a used a washing step to remove labile organic matter, which consistently gave lower results (Supplement 2). However, it has been shown that the majority of hydrophobic soot-BC may be lost during this ex situ washing (Elmquist *et al*., 2004).

3.8.2. Method BPCA

Advantages: Method BPCA is the method best suited for identifying BC components in solution. This molecular marker method also provides information on the nature of BC beyond just an estimation of the amount, as it identifies and quantifies a number of BC markers that can be related to source and formation conditions of the BC.

Disadvantages: This method is also prone to positive biases from non-BC materials, notably from the shale (average 4.1% BC/OC) and coals (15.6-20.9% BC/OC). Interlaboratory reproducibility should be improved by further standardization, as BC concentrations reported by the three different laboratories that used this

technique varied by a factor of at least two for six of the twelve samples analyzed, and these variations were inconsistent (different laboratories reported the highest values for different samples). The BC values for the soot and chars were quite low, suggesting that the technique does not quantitatively recover the largest and most condensed BC components as BPCAs. To account for the incomplete conversion of BC to BPCAs, results were corrected with a factor, empirically determined by referencing to commercial charcoal (2.27) (Glaser *et al*., 1998). However, results from the measurement of other types of BC char materials suggested that using this factor only gives a conservative, minimum estimate of BC found, and is currently disputed (Brodowski *et al*., 2005b).

3.8.3. Method Cr_2O_7

Advantages: This method probably requires the least expensive or specialized equipment and so can be carried out in most laboratories. Reproducibility was reasonably good for the soot, char and bituminous coal samples, with all reported BC values within a factor of two.

Disadvantages: This method assumes that all of the carbon that survives the oxidation treatment is BC, but recorded 9.6% BC/OC for the shale and 14.7-85.0% BC/OC for the coals. This assumption has also elsewhere been shown to be invalid in at least some cases where kerogen has been isolated along with black carbon (Song *et al*., 2002; Masiello, 2004). This problem could be overcome characterizing the residue by solid-state NMR spectroscopy, as is done for the related chemical oxidation methods NaClO and UV. However, this would increase the complexity and cost of the technique, as enough material would need to be isolated for NMR analysis. The residue would need to be pretreated for NMR analysis (e.g. with HF), NMR itself is expensive, and the paramagnetic Cr may also interfere with the NMR analysis. Reproducibility was not so good for the sediment and soil samples, with BC concentrations reported by the four different laboratories that used this technique varying by a factor of at least three for these samples.

3.8.4. Method TOT/R

Advantages: Both intra- and inter-lab variability was lower than for the other methods for most samples. The method thermally discerns between organic carbon and black (elemental) carbon, although it was not equally successful for all materials tested here. Only further testing can determine if this method could be used in soil and sediment studies.

Disadvantages: The method did not provide adequate differentiation between BC and non-BC organic matter (as defined for soil and sediment studies), as exemplified by the very high BC values reported for DOM, melanoidin and coals (Figure 2). Care has to be taken to effectively remove the inorganic matrix of soils and sediments that can lead to interferences, e.g. premature charring. In addition, higher loaded (darker) samples probably create problems in the optical corrections procedures, when the absorption is so high that an additional blackening by charring during pyrolysis cannot be discriminated from the original absorption signal (Schmid *et al*., 2001). This method normally requires that the material, with little or no inorganic matrix, be collected on a filter paper *in situ*. Resuspension of bulk materials like soils and sediments are possible but care should be taken to spread the sample as thinly and homogeneously as possible.

3.8.5. Method TG-DSC

Advantages: This method has the advantage that it is operationally very simple, and that it can detect all carbon species (including carbonates, oxalate) within a sample. In this trial, the BC values reported for the soot, chars and potentially interfering materials are in agreement with other methods for nine of the 12 samples. Disagreement arose as a consequence of mineral impurities, especially clays, in the environmental materials.

Disadvantages: This method may overestimate BC in samples with low C contents (i.e. most sediments and soils) if certain impurities are present (Dell'Abate et al., 2003, Lopez-Capel et al., 2005), but also non-BC materials with high carbon contents like the coals (19.0-92.5% BC/OC; again, mineral contaminants may be present). Thermogravimetry measures the total weight loss during a heating profile. Therefore, mineral impurities such as clays will contribute to the measured weight loss as they lose water on heating. This may be the reason why this method gave the highest BC values for the aerosol, marine sediment and soil samples (Figure 2, Supplement 2). If calcite ($CaCO_3$) is present, it can be distinguished from BC as it decomposes at higher temperatures, allowing each to be quantified separately (Manning *et al*., 2005). Pretreatment to increase the

concentration of organic matter (such as HF-treatment or physical separation) may overcome the problem of impurities, and techniques such as X-ray diffraction should be used to determine independently whether or not mineral impurities are present. This technique was used by only one laboratory and no replicate measurements were made, for these specific samples; reproducibility is generally within 5%. This technique shows promise, but needs to be tested on a larger range of samples, and in other laboratories.

3.8.6. Method NaClO

Advantages: This method and method A were the only ones that selectively detected soot.

Disadvantages: This method was used by only one laboratory, and results were only provided for seven of the twelve samples. This technique shows promise, but needs to be tested on a larger range of samples, and in other laboratories. However, NMR quantification is expensive.

3.8.7. Method UV

Advantages: This method detects BC across most of the BC continuum. The UV photo-oxidation appears to be "gentler" on BC than the alternative chemical oxidation methods (Cr_2O_7 and NaClO), as evidenced by the higher BC values reported for the soot and chars (Figure 2). This method has been used extensively to quantify BC in soils, and the BC fraction isolated using this method has been shown to turnover slowly in soils (Skjemstad *et al*., 2001; 2004).

Disadvantages: Positive biases from the coals (26.9-94.3% BC/OC) were recorded with this method. Method UV was used by only one laboratory, and without replication, so it was not possible to gauge intra- or inter-laboratory reproducibility. It uses a specialized, home-built photo-oxidation apparatus, which is not easy to replicate. The method is also time-consuming and expensive.

4. BC quantification – where to next?

While there have been many intercomparisons of BC quantification for atmospheric samples, this is the first ever wide-ranging intercomparison of BC measurements for soils and sediments. This exercise was not limited to a single sample (as in Currie et al, 2002), a single method or a single lab but a much larger effort on behalf of our community. This work may be a first, essential step in filling the gaps in the terrestrial compartment of the global BC budget. Although we lack enough information to interconvert measurements made in a variety of matrices (atmosphere, ocean, soils, sediments), we lay the groundwork for continued method validation, which will make possible the combination of datasets generated in different environments. At present we do not have enough analytical information to assess the quantitative importance in environmental matrices but we can point out several observations, some of which are also highlighted in the conceptual summary (Figure 1, lower part).

a. Reproducibility within laboratories was often in the typical range observed when analyzing environmental samples, e.g. soil amino acids: 5 % CV (Stevenson, 1996). However, reproducibility among laboratories using nominally the same method was not satisfactory. This shows that these methods were sensitive to variations in analytical procedures. Standardization of methods (e.g. temperatures and acid strengths) will decrease variability within methods. However, before standard conditions can be agreed upon, we must determine which conditions give the "best" results. This will not be a simple decision, as there is scope for both under- and over-estimation of BC. Therefore, it is not a simple case of choosing which conditions provide the highest or lowest BC values for a given sample. It may also be that different sets of conditions are appropriate for different sample types or different applications. Method refinement will be a continuing feature of BC quantification in the foreseeable future.

b. The TOT/R method is widely used for measuring atmospheric OC/EC concentrations on filter samples. It is important to note that the samples used in this intercomparison exercise were not provided in a manner (i.e., as solids on filters) similar to typical aerosol collections. Such aerosol analyses are predicated on collecting particles on a filter *in situ*. We found that attempts to replicate this by resuspending the samples and then filtering were not successful. As a thermal oxidation method, it can potentially be used to quantify BC in soils and sediments, but would need to be adapted to deal with the problems of transmittance and reflectance related to dark materials, as well as inorganic matrices associated with soils and sediments. Worldwide atmospheric observation networks rely on TOT/R data to link atmospheric BC to climate change through the

optical properties of the carbonaceous aerosols. Thus, this method best serves the environmental community in the capacity for which is was developed.

c. The current definition of BC is imprecise. It is variously used to describe either a whole range or spectrum of materials, or only parts of it. Therefore, it is not possible to identify a "correct" or "true" BC content for each of the reference materials. However, this is not to say that every method produces an equally valid value. There are two causes of the divergent values of BC content: (i) differing sensitivity to differing BC types and (ii) under- and over-estimation of BC due to methodological differences or problems. All of the methods may be subject to the latter, though probably to differing extents. There is a clear need for users of each method to determine the nature, cause and magnitude of these problems.

d. A complete accounting of the global black carbon budget is compounded by the fact that results from the different methods investigated here did not have consistent values across methods, implying that there is no commonality or simple correlation factors among methods *per se*. This is to be expected when each BC method is selective for a different part of the BC continuum, for example, soot or highly condensed wood char or more amorphous wood char. For example, for a sample with a 2:1 mixture of char to soot, a factor of 2 difference between methods does not necessarily mean that one method detects only half of the total BC pool; it could simply indicate that one method quantitatively detected the soot third of the pool, while the other quantitatively detected the 2/3 of the pool composed of wood char.

e. The ultimate value of the various BC quantification methods is not how they compare to one another, but whether they provide useful information for the application for which they are used. BC quantification is not an end in itself, but rather a means to an end. On this criterion, each of the methods has already proven its value. For example, BC contents determined using the CTO-375 method correlated with other combustion markers like polycyclic aromatic hydrocarbons (PAHs) (Gustafsson *et al*., 1997; Gustafsson and Gschwend, 1998; Persson *et al*., 2002; Reddy *et al*., 2002) and the BC fraction isolated UV-photo-oxidation (UV) has been shown to turnover slowly in soils (Skjemstad *et al*., 2001; 2004).

f. To improve comparability between laboratories using the same method and between different methods, we strongly recommend that future BC studies include evaluation of all methods against the set of BC reference materials analyzed here. This recommendation also holds true for future methodological improvements, and the development of novel analytical approaches to quantify BC in environmental samples. Samples outside the set of twelve reference materials used here can also play a role in future BC method evaluation. We recommend the use of well-characterized, environmentally relevant and readily accessible diesel soot standards from NIST (e.g. SRM 2975). The diesel soot SRM 2975 has been used in numerous studies to quantify BC and complement the laboratory-produced n-hexane soot as well as the urban dust, which contains among other things diesel soot from fossil fuel burning (Gustafsson *et al*., 2001; Elmquist *et al*., 2004; Nguyen *et al*., 2004b; Currie and Kessler, 2005). Specially prepared filter samples of atmospheric samples such as the prototype filter reference material prepared for the intercomparison of the urban dust in a separate study (Currie *et al*., 2002) can be useful to limit errors when using the TOT/R method. One or two other "negative controls", apart from the melanoidin used here would be useful additions. We do however emphasize the advantages of using the twelve reference materials studied here: (i) their ready availability and (ii) the existence of this extensive comparative study data set.

Acknowledgements

Inspiration and encouragement to pursue this ring trial came from the late John Hedges.

References

Andreae, M.O. and Gelencsér, A. (2006), Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols. *Atmos. Chem. Phys., 6,* 3131-3148.

Akhter, M.S., A.R. Chughtai, and D.M. Smith (1985), The structure of hexane soot I: Spectroscopic studies. *Appl. Spectrosc.*, *39(1),* 143-153.

Baldock, J.A., and R.J. Smernik (2002), Chemical composition and bioavailability of thermally altered

Pinus resinosa (Red pine) wood, *Org. Geochem*., *33*, 1093-1109.

Benzing-Purdie, L. and J.A. Ripmeester (1983), Melanoidins and soil organic matter – evidence of strong similarities revealed by C-13 CP-MAS NMR, *Soil Sci. Soc. Am. J.*, *47(1)*, 56-61.

Birch, M.E. and R.A. Cary (1996), Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. *Aerosol Sci. Technol*., *25(3),* 221-241.

Bird, M.I., and D.R. Gröcke (1997), Determination of the abundance and carbon isotope composition of elemental carbon in sediments, *Geochim. Cosmochim. Acta*, 61, 3413-3423.

Brodowski S., W. Amelung, L. Haumaier, C. Abetz, W. Zech (2005a), Morphological and chemical properties of black carbon in physical soil fractions as revealed by scanning electron microscopy and energy-dispersive X-ray spectroscopy. *Geoderma,* 128, 116-129.

Brodowski, S., A. Rodionov, L. Haumaier, B. Glaser, W. Amelung (2005b), Revised black carbon assessment using benzene polycarboxylic acids, *Org. Geochem*., *36*, 1299-1310.

Chen, Y., G. Sheng, X. Bi, Y. Feng, B. Mai, and J. Fu (2005), Emission factors for carbonaceous particles and polycyclic aromatic hydrocarbons from residential coal combustion in China, *Environ. Sci. Technol*., *39*, 1861-1867.

Chow, J.C., J.G. Watson, L.C. Pritchett, W.R. Pierson, C.A. Frazier, and R.G. Purcell (1993), The DRI Thermal/Optical Reflectance carbon analysis system: Description, evaluation and applications in U.S. air quality studies. *Atmos. Environ. 27A (8),* 1185-1201.

Chow, J.C., J.G. Watson, L.-W. A. Chen, W.P. Arnott, and H. Moosmüller (2004), Equivalence of elemental carbon by thermal/optical reflectance and transmittance with different temperature protocols, *Environ. Sci. Technol.*, *38*, 4414-4422.

Crutzen, P.J. and M.O. Andreae (1990), Biomass burning in the tropics: impact on atmospheric chemistry and biogeochemical cycles. *Science 250*, 1669-1678.

Currie, L. A. and J.D. Kessler (2005), On the isolation of elemental carbon (EC) for micro-molar 14C accelerator mass spectrometry: development of a hybrid reference material for 14C-EC accuracy assurance, and a critical evaluation of the thermal optical kinetic (TOK) EC isolation procedure. *Atmos. Chem. Phys.*, *5*, 2833-2845.

Currie, L.A., J.B.A. Benner, J.D. Kessler, D.B. Klinedinst, G.A. Klouda, J.V. Marolf, J.F. Slater, S.A. Wise, H. Cachier, R. Cary, J.C. Chow, J. Watson, E.R.M. Druffel, C.A. Masiello, T.I. Eglinton, A. Pearson, C.M. Reddy, Ö. Gustafsson, P.C. Hartmann, J.G. Quinn, J.I. Hedges, K.M. Prentice, T.W. Kirchstetter, T. Novakov, H. Puxbaum, and H. Schmid (2002), A critical evaluation of interlaboratory data on total, elemental, and isotopic carbon in carbonaceous particle reference material, NIST SRM 1649a, *J. Nat. Int. Std. Technol*., *107*(3), 279-298.

Czimczik, C.I., C.M. Preston, M.W.I. Schmidt, R.A. Werner, and E.-D. Schulze (2002), Effect of charring on mass, organic carbon, and stable carbon isotope composition of wood, *Org. Geochem*., *33*, 1207-1223.

Dell'Abate, M.A., A. Benedetti, and P. Sequi (2000), Thermal methods of organic matter maturation monitoring during a composting process, *J. Therm. Anal. Calorim*., 61, 389-396.

Dell'Abate, M.A., A. Benedetti, and P.C. Brookes (2003), Hyphenated techniques of thermal analysis for characterisation of soil humic substances, *J. Sep. Sci*., 26, 433-440.

Elmquist, M., Ö. Gustafsson, and P. Andersson (2004), Quantification of sedimentary black carbon using the chemothermal oxidation method: an evaluation of ex situ pretreatments and standard additions approach, *Limnol Oceanogr-Meth*., *2*, 417-427.

Elmquist, M., G. Cornelissen, Z. Kukulska, and Ö. Gustafsson (2006), Distinct oxidative stabilities of char versus soot black carbon: Implications for quantification and environmental recalcitrance, *Global Biogeochem. Cy*., *20*, GB2009, doi:10.1029/2005GB002629.

Fernandes, M.B., J.O. Skjemstad, B.B. Johnson, J.D. Wells, and P. Brooks (2003), Characterization of carbonaceous combustion residues. I. Morphological elemental and spectroscopic features, *Chemosphere*, *51*, 785-795.

Forbes, M.S., R.J. Raison and J.O. Skjemstad (2006), Formation, transformation and transport of black carbon (charcoal) in terrestrial and aquatic ecosystems. *Sci. Total Environ.* 370, 190-206.

Gélinas, Y., K.M. Prentice, J.A. Baldock, and J.I. Hedges (2001), An improved thermal oxidation method for the quantification of soot/graphitic black carbon in sediments and soils, *Environ. Sci. Technol*., *35*(17), 3519-3525.

Glaser, B., L. Haumaier, G. Guggenberger, and W. Zech (1998), Black carbon in soils: the use of benzenecarboxylic acids as specific markers, *Org. Geochem*., *29*(49, 811-819.

Goldberg, E.D. (1985), Black carbon in the environment, 198 pp., John Wiley & Sons, Inc., New York.

Gustafsson, Ö. and P.M. Gschwend (1997), Soot as a strong partition medium for polycyclic aromatic hydrocarbons in aquatic systems, *ACS Sym Ser*., *671*, 365-381.

Gustafsson, Ö., and P.M. Gschwend (1998), The flux of black carbon to surface sediments on the New England continental shelf, *Geochim. Cosmochim. Acta*, *62*, 465-472.

Gustafsson, Ö., F. Haghseta, C. Chan, J. Macfarlane, and P.M. Gschwend (1997), Quantification of the dilute sedimentary soot phase: Implications for PAH speciation and bioavailability, *Environ. Sci. Technol*., *31*, 203-209.

Gustafsson, Ö., T.D. Bucheli, Z. Kukulska, M. Andersson, C. Largeau, J.-N. Rouzaud, C.M. Reddy, and T.I. Eglinton (2001), Evaluation of a protocol for the quantification of black carbon in sediments, *Global Biogeochem. Cy*., *15*(4), 881-890.

Hammes, K., R.J. Smernik., J.O. Skjemstad, A. Herzog, U.F. Vogt, and M.W.I. Schmidt (2006), Synthesis and characterisation of laboratory-charred grass straw (*Oryza sativa*) and chestnut wood (*Castanea sativa*) as reference materials for black carbon quantification, *Org. Geochem*., 37, 1629-1633.

Hedges, J.I., G. Eglinton, P.G. Hatcher, D.L. Kirchman, C. Arnosti, S. Derenne, R.P. Evershed, I. Kögel-Knabner, J.W. de Leeuw, R. Littke, W. Michaelis, and J. Rullkötter (2000), The molecularly-uncharacterized component of nonliving organic matter in natural environments, *Org. Geochem*., *31*, 945-958.

Hockaday, W. C. H., Grannas, A. M., Kim, S., and P.G. Hatcher (2006). Direct molecular evidence for the degradation and mobility of black carbon in soils from ultrahigh-resolution mass spectral analysis of dissolved organic matter from a fire-impacted forest soil, *Org. Geochem.*, 37, 501-510.

Huang, L., J.R. Brook, W. Zhang, S.M. Li, L. Graham, D. Ernst, A. Chiculescu, and G. Lu (2006), Stable isotope measurements of carbon fractions (OC/EC) in airborne particulate: A new dimension for source characterization and apportionment, *Atmos. Environ*., *40*(15), 2690-2705.

Huebert, B.J., T. Bertram, J. Kline, S.G. Howell, D. Eatough, and B. Blomquist (2004), Measurements of organic and elemental carbon in Asian outflow during ACE-Asia from the NSF/NCAR C-130, *J. Geophys. Res*., *109*, D19S11, doi:10.1029/2004JD004700.

Jonker, M.T.O. and A.A. Koelmans (2002), Sorption of polycyclic aromatic hydrocarbons and polychlorinated biphenyls to soot and soot-like materials in the aqueous environment: mechanistic considerations, *Environ. Sci. Technol*., *36*(36), 3725-3734.

Kuhlbusch, T.A.J., M.O. Andreae, H. Cachier, J.G. Goldammer, J.-P. Lacaux, R. Shea, and P.J. Crutzen (1996), Black carbon formation by savanna fires: Measurements and implications for the global carbon cycle, *J. Geophys. Res*., *101*, 23651-23665.

Lim. B., and H. Cachier (1996), Determination of black carbon by chemical oxidation and thermal treatment in recent marine and lake sediments and Cretaceous-Tertiary clays, *Chem. Geol*., *131*, 143-154.

Lopez-Capel, E., S.P. Sohi, J.L. Gaunt, and D.A.C. Manning (2005), Use of thermogravimetry-differential scanning calorimetry to characterize modelable soil organic matter fractions, *Soil Sci. Soc. Am. J*., *69(1)*, 136-140.

Manning, D.A.C., E. Lopez-Capel, and S. Barker (2005), Seeing soil carbon, use of thermal analysis in the characterization of soil C reservoirs of differing stability, *Mineral. Mag*., *69(4),* 425-435.

Masiello, C.A. (2004), New directions in black carbon organic geochemistry, *Mar. Chem*., *92*, 201-213.

Masiello, C.A., E.R.M. Druffel, and L.A. Currie (2002), Radiocarbon measurements of black carbon in aerosols and ocean sediments, *Geochim. Cosmochim. Acta, 66(6)*, 1025-1036.

Nguyen, T.H., R.A. Brown, and W.P. Ball (2004a), An evaluation of thermal resistance as a measure of black carbon content in diesel soot, wood char, and sediment, *Org. Geochem*, *35*, 217-234.

Nguyen, T.H., I. Sabbah, and W.P. Ball (2004b), Sorption nonlinearity for organic contaminants with diesel soot: Method development and isotherm interpretation, *Environ. Sci. Technol*., *38*, 3595-3603.

NIST (2001), Certificate of analysis, Standard Reference Material (SRM) 1649a, Urban dust. National Institute of Standards and Technology, Gaithersburg, MD.

NIST (2004), Certificate of Analysis, Standard Reference Material (SRM) 1941b, Organics in marine sediment. National Institute of Standards and Technology, Gaithersburg, MD.

Novakov, T. (1984), The role of soot and primary oxidants in atmospheric chemistry, *Sci. Total Environ*., *36*, 1-10.

Persson, N.J., Ö, Gustafsson, T.D. Bucheli, R. Ishaq, K. Naes, and D. Broman (2002), Soot-carbon influenced distribution of PCDD/Fs in the marine environment of the Grenlandsfjords, Norway, *Environ. Sci. Technol*., *36(23), 4968-4974.*

Petsch, S.T., R.J. Smernik, T.I. Eglinton, and J.M. Oades (2001), A solid-state ^{13}C-NMR study of

kerogen degradation during black shale weathering. *Geochim. Cosmochim.Acta*, *65(12),* 1867-1882.

Plante, A.F., M. Pernes, and C. Chenu (2005), Changes in clay-associated organic matter quality in a C depletion sequence as measured by differential thermal analyses, *Geoderma*, 129, 186-199.

Poirier, N., S. Derenne, J.-N, Rouzaud, C. Largeau, A. Mariotti, J. Balensdent, and J. Maquet (2000), Chemical structure and sources of macromolecular, resistant, organic fraction isolated from a forest soil (Lacadée, south-west France), *Org. Geochem.*, *31*, 813-827.

Poirier, N., S. Derenne, J. Balensdent, J.-N, Rouzaud, A. Mariotti, and C. Largeau (2002), Abundance and composition of the refractory organic fraction of an ancient, tropical soil (Pointe Noire, Congo), *Org. Geochem.*, *33*, 383-391.

Preston, C.M. and M.W.I. Schmidt (2006), Black (pyrogenic) carbon: a synthesis of current knowledge and uncertainties with special consideration of boreal regions, *Biogeoscience 3*, 397-420.

Reddy, C.M., A. Pearson, L. Xu, A.P. McNichol, B.A. Benner Jr., S.A. Wise, G.A. Klouda, L.A. Currie, and T.I. Eglinton (2002), Radiocarbon as a tool to apportion the sources of polycyclic aromatic hydrocarbons and black carbon in environmental samples, *Environ. Sci. Technol.*, *36(8)*, 1774-1782.

Rumpel, C., M. Alexis, A. Chabbi, V. Chaplot, D.P. Rasse, C. Valentin, and A. Mariotti (2006), Black carbon contribution to soil organic matter composition in tropical sloping land under slash and burn agriculture, *Geoderma*, 130, 35-46.

Schauer, J.J., B.T. Mader, J.T. Deminter, G. Heidemann, M.S. Bae, J.H. Seinfeld, R.C. Flagan, R.A. Cary, D. Smith, B.J. Huebert, T. Bertram, S. Howell, J.T. Kline, P. Quinn, T. Bates, B. Turpin, H.J. Lim, J.Z. Yu, H. Yang, and M.D. Keywood (2003), ACE-Asia intercomparison of a thermal-optical method for the determination of particle-phase organic and elemental carbon, *Environ. Sci. Technol.*, *37*, 993-1001.

Schmid, H., L. Laskus, H.J. Abraham, U. Baltensperger, V. Lavanchy, M. Bizjak, P. Burba, H. Cachier, D. Crow, J. Chow, T. Gnauk, A. Even, H.M.T. Brink, K.-P. Giesen, R. Hitzenberger, C. Hueglin, W. Maenhaut, C. Pio, A. Carvalho, J.-P. Putaud, D. Toom-Sauntry, and H. Puxbaum (2001), Results of the "carbon conference" international aerosol carbon round robin test Stage I, *Atmos. Environ.*, *35*, 2111-2121.

Schmidt, M.W.I., and A.G. Noack (2000), Black carbon in soils and sediments: Analysis, distribution, implications, and current challenges, *Global Biogeochem. Cy.*, *14*, 777-794.

Schmidt, M.W.I., J.O. Skjemstad, C.I. Czimczik, B. Glaser, K.M. Prentice, Y. Gelinas, and T.A.J. Kuhlbusch (2001), Comparative analysis of black carbon in soils, *Global Biogeochem. Cy.*, *15*, 163-167.

Schmidt, M.W.I., J.O. Skjemstad, and C. Jäger (2002), Carbon isotope geochemistry and nano-morphology of soil black carbon: Black Chernozemic soils in Central Europe originate from ancient biomass burning. *Global Biogeochem. Cy. 16(4),* 1123 (doi:10.1029/2002GB001939).

Schmidt, M.W.I., C.A. Masiello, and J.O. Skjemstad (2003), Final recommendations for reference materials in black carbon analysis, *EOS Trans. AGU*, *84*(52), 582-583.

Serkiz, S.M. and E.M. Perdue (1990), Isolation of dissolved organic matter from the Suwannee River using reverse osmosis. *Water Res.*, *24(7),* 911-916.

Sharma, R.K., J.B. Wooten, V.L. Baliga, X. Lin, W.G. Chan, and M.R. Hajaligol (2004), Characterization of chars from pyrolysis of lignin, *Fuel*, *83*, 1469-1482.

Simpson, M.J., and P.G. Hatcher (2004a), Determination of black carbon in natural organic matter by chemical oxidation and solid-state 13C nuclear magnetic resonance spectroscopy, *Org. Geochem.*, *358*, 923-935.

Simpson, M.J., and P.G. Hatcher (2004b), Overestimations of black carbon in soils and sediments, *Naturwissenschaften*, *91*, 436-440.

Skjemstad, J.O., P. Clarke, J.A. Taylor, J.M. Oades, and S.G. McClure (1996), The chemistry and nature of protected carbon in soil, *Aust. J. Soil Res.*, *34*, 251-271.

Skjemstad, J.O., J.A. Taylor, and R.J. Smernik (1999), Estimation of charcoal (char) in soils, *Commun. Soil Sci. Plan*, *30*, 2283-2298.

Skjemstad, J.O., R.C. Dalal, L.J. Janik, and J.A. McGowan (2001), Changes in chemical nature of soil organic carbon in Vertisols under wheat in south-eastern Queensland, *Aust. J. Soil Res.*, *39*, 343-359.

Skjemstad, J.O., L.R. Spouncer, B. Cowie, R.S. Swift (2004), Calibration of the Rothamsted organic carbon turnover model (RothC ver. 26.3), using measurable soil organic carbon pools, *Aust. J. Soil Res.*, *42*, 79-88.

Smith, D.M. and A.R. Chughtai (1995), The surface structure and reactivity of black carbon. *Coll. Sur. A*, *105(1*), 47-77.

Song, J., P. Peng, and W. Huang (2002), Black carbon and kerogen in soils and sediments. 1. Quantification and characterization, *Environ. Sci. Technol.*, *36*, 3960-3967.

Stevenson, F.J. (1996), Nitrogen-organic forms, in *Methods of soil analysis, Part 3*, Soil Science Society of America Book Series, edited by D.L. Sparks, pp. 1185-1200, Soil Sci. Am. Inc., Am. Soc. Agron. Inc., Madison.

Trewhella, M.J., I.J.F. Poplett and A. Grint (1986), Structure of Green River oil-shale kerogen – determination using solid-state C-13 NMR-Spectroscopy, *Fuel*, *65*, 541-546.

Vorres, K. (1990), The Argonne Premium Coal Sample Program, *Energ. Fuel*, *4*, 420-426.

Watson, J.G., J.C. Chow, and L.-W.A. Chen (2005), Summary of organic and elemental carbon/black carbon analysis methods and intercomparisons, *Aerosol Air Qual. Res*., 5, 65-102.

Wolbach, W.S. and E. Anders (1989), Elemental carbon in sediments: determination and isotopic analysis in the presence of kerogen, *Geochim. Cosmochim. Acta*, 53, 1637-1647.

Youden, W.J. (1959), Graphical diagnosis of interlaboratory test results, *Ind. Qual. Control*, 15, 24-28.

Supporting online material

Supplement 1 List of laboratories with names of participants and affiliations in laboratory number order

Supplement 2 Black carbon concentrations (g kg^{-1}) as measured by different laboratories

Supplement 1

List of laboratories with names of participants and affiliations in laboratory number order

1 - William P. Ball, Marie Fukudome, Thanh. H. Nguyen
Department of Geography and Environmental Engineering, Johns Hopkins University, USA

2 - Wulf Amelung, Sonja Brodowski
Institute of Crop Science and Resource Conservation, Division of Soil Science, University of Bonn, Bonn, Germany

3 - Luyi Ding
Analysis and Air Quality Division, Environmental Technology Center, Ontario, Canada

4 - Francisco J. Gonzalez-Vila, José A. Gonzalez-Perez, José M. de la Rosa
Department Biogeoquímica y Dinámica de Contaminantes, Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS-CSIC), Spain

Lopez-Capel Elisa, David A.C. Manning

School of Civil Engineering and Geosciences, University of Newcastle upon Tyne, Newcastle, UK

5 - Philip M. Gschwend, Xanat Flores
R.M. Parsons Laboratory, MIT 48-413, Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Massachusetts, USA

6 - Georg Guggenberger, Klaus Kaiser, Andrei Rodionov
Institute for Soil Science and Plant Nutrition, Martin Luther University, Halle-Wittenberg, Germany

7 - Orjan Gustafsson, Marie Elmquist, Gerard Cornelissen
Department of Applied Environmental Science (ITM), Stockholm University, Stockholm, Sweden

8 - Patrick G. Hatcher, William C. Hockaday
Environmental Molecular Science Institute, Ohio State University, Columbus, USA

9 - Lin Huang, Wendy Zhang
Air Quality Research Division, Atmospheric Science and Technology Directorate, Science & Technology Branch, Environment Canada, Canada

10 - Barry J. Huebert
Department of Oceanography, University of Hawaii, USA

11 - Claude Largeau, Jean-Noël Rouzaud
Laboratoire de Chimie Bioorganique et Organique Physique, Ecole Nationale Supérieure de Chimie de Paris, Paris, France

Cornelia Rumpel
Laboratoire de Géologie, Ecole Normale-Supérieure, Paris, France

12 - Patrick Louchouarn, Stephane Houel
Department of Earth and Environmental Sciences, Lamont-Doherty Earth Observatory, Columbia University, New York, USA

13 - Siddhartha Mitra, Joshua C. Dunn
Department of Geological Sciences and Environmental Studies, Binghamton University, Binghamton, New York, USA

14 - Michael W. I. Schmidt, Karen Hammes
Department of Geography, University of Zurich, Zurich, Switzerland

15 - Jan O. Skjemstad
CSIRO Land and Water, Glen Osmond, Australia

Ronald J. Smernik
Soil and Land Systems, School of Earth and Environmental Sciences, University of Adelaide, Waite Campus, Urrbrae, Australia

16 - Jianzhong Song, Ping'an Peng
State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, P.R. China

17 - Christoph Hartkopf-Froeder, Axel Boehmer, Burkhard Leuer
Geologischer Dienst NRW, Krefeld, Germany

Supplement 2

Table 1. Black carbon concentrations of the environmental matrices for individual teams, grouped according to method employed (g kg^{-1} mass). Bold type numbers are over all the teams in the method.

Lab	Aerosol					Marine sediment					Vertisol					Chernozem					DOM				
	[a] BC	[b] *s*	[c] *n*	[d] *u*	[e] *CV*	BC	*s*	*n*	*u*	*CV*	BC	*s*	*n*	*u*	*CV*	BC	*s*	*n*	*u*	*CV*	BC	*s*	*n*	*u*	*CV*
A. Thermal oxidation method (CTO-375)																									
1	13.7	*0.8*	*6*	*0.3*	*5.8*	5.4	*0.3*	*5*	*0.3*	*5.6*	1.3	*0.5*	*6*	*0.2*	*38.5*	1.6	*0.2*	*5*	*0.1*	*12.5*	4.4	*2.2*	*5*	*1.0*	*50.0*
5	25.9	*1.1*	*3*	*0.6*	*4.2*	7.4	*0.2*	*3*	*0.2*	*2.7*	1.3	*0.1*	*3*	*0.1*	*7.7*	1.0	*0.1*	*3*	*0.1*	*10.0*	0.0	-	*3*		-
7a	18.3	*0.3*	*3*	*0.2*	*1.6*	5.7	*0.3*	*3*	*0.2*	*5.3*	0.8	*0.0*	*3*	*0.0*	*0.0*	0.5	*0.1*	*3*	*0.1*	*20.0*	0.8	*0.1*	*3*	*0.1*	*12.5*
7b	15.8	*0.8*	*15*	*0.1*	*5.1*	3.8	*0.7*	*15*	*0.2*	*18.4*	-	-	-		-	-	-	-		-	-	-	-		-
12a	6.4	*0.7*	*3*	*0.4*	*10.9*	4.1	*0.8*	*5*	*0.4*	*19.5*	0.1	*0.0*	*2*	*0.0*	*10.0*	0.2	*0.0*	*2*	*0.0*	*5.0*	0.0	*0.0*	*2*	*0.0*	-
12b	9.0	-	*1*		-	4.1	*0.4*	*6*	*0.2*	*9.8*	0.5	-	*1*		-	0.5	-	*1*		-	0.4	-	*1*		-
Average	**14.9**					**5.1**					**0.8**					**0.8**					**1.1**				
n	**6**					**6**					**5**					**5**					**5**				
s	**7.0**					**1.4**					**0.5**					**0.6**					**1.9**				
B. Molecular markers method (BPCA)																									
2	17.7	*3.2*	*3*	*1.8*	*18.1*	2.8	*1.2*	*2*	*0.9*	*42.9*	5.1	*0.5*	*2*	*0.3*	*9.2*	2.7	*0.52*	*2*	*0.4*	*19.3*	2.8	*0.8*	*4*	*0.4*	*30.0*
6	-	-	-		-	-	-	-		-	6.8	*1.0*	*3*	*0.6*	*14.8*	4.4	*1.0*	*2*	*0.7*	*22.5*	-	-	-		-
14	11.2	*0.7*	*3*	*0.4*	*6.6*	0.6	*0.2*	*2*	*0.1*	*31.7*	2.9	*0.5*	*3*	*0.3*	*18.8*	4.4	*0.2*	*3*	*0.1*	*5.5*	38.2	*6.8*	*2*	*4.8*	*17.8*
Average	**14.5**					**1.7**					**4.9**					**3.8**					**20.5**				
n	**2**					**2**					**3**					**3**					**2**				
s	**4.5**					**1.5**					**1.9**					**1.0**					**25.1**				
C. Acid dichromate oxidation (Cr_2O_7)																									
11	40.2	*0.3*	*2*	*0.2*	*0.7*	3.7	*3.4*	*2*	*2.4*	*91.9*	1.1	*0.5*	*2*	*0.4*	*45.5*	0.7	*0.1*	*2*	*0.1*	*14.3*	-	-	-		-
13	79.4	-	*1*		-	19.9	*7.9*	*5*	*3.5*	*39.7*	5.67	*2.0*	*3*	*1.2*	*35.3*	2.1	*0.5*	*4*	*0.3*	*24.0*	-	-	-		-
16b	72.1	*3.1*	*3*	*1.8*	*4.3*	11.7	*0.4*	*3*	*0.2*	*3.4*	4.0	*0.2*	*3*	*0.1*	*5.0*	2.2	*0.1*	*3*	*0.1*	*4.5*	0.0	-	*3*		-
17	-	-	-		-	12.0	-	*1*		-	8.0	-	*1*		-	0.6	-	*1*		-	-	-	-		-
Average	**63.9**					**11.8**					**4.7**					**1.4**									
n	**3**					**4**					**4**					**4**									
s	**20.8**					**6.6**					**2.9**					**0.9**									

Table 1 (continued). Black carbon concentrations of the environmental matrices for individual teams, grouped according to method employed (g kg^{-1} mass). Bold type numbers are over all the teams in the method.

Lab	Aerosol					Marine sediment					Vertisol					Chernozem					DOM				
	BC	*s*	*n*	*u*	*CV*	BC	*s*	*n*	*u*	*CV*	BC	*s*	*n*	*u*	*CV*	BC	*s*	*n*	*u*	*CV*	BC	*s*	*n*	*u*	*CV*
D. Thermal/optical reflectance and transmittance method (TOR/TOT)																									
3	62.6	*10.0*	*3*	*5.76*	*15.9*	3.2	*0.7*	*3*	*0.38*	*20.3*	7.4	*0.6*	*3*	*0.3*	*8.0*	4.3	*0.8*	*3*	*0.5*	*19.5*	89.6	*11.9*	*3*	*6.8*	*13.2*
9a	89.2	*1.5*	*3*	*0.87*	*1.7*	16.4	*0.6*	*3*	*0.35*	*3.7*	10.9	*0.6*	*3*	*0.3*	*5.5*	6.3	*0.3*	*3*	*0.2*	*4.8*	309.8	*1.8*	*3*	*1.0*	*0.6*
9b	86.1	*0.8*	*3*	*0.46*	*0.9*	16.1	*0.6*	*3*	*0.35*	*3.7*	10.8	*0.7*	*3*	*0.4*	*6.5*	0.0	*0.1*	*3*	*0.1*	-	295.0	*16.9*	*3*	*9.8*	*5.7*
[f]10	46.0	-	*3*		-	-	-	-		-	6.0	-	*3*		-	6.0	-	*3*		-	0.0	-	*3*		-
16a	48.5	*1.1*	*3*	*0.64*	*2.3*	8.0	*0.2*	*3*	*0.12*	*2.5*	6.6	*0.1*	*3*	*0.1*	*1.5*	3.1	*0.1*	*3*	*0.1*	*3.2*	117.1	*0.5*	*3*	*0.3*	*0.4*
Average	**66.5**					**10.9**					**8.3**					**3.9**					**162.3**				
n	**5**					**4**					**5**					**5**					**5**				
s	**20.4**					**6.5**					**2.3**					**2.6**					**135.1**				
Other independent methods (4 = E: Thermogravimetry (TG-DSC), 8 = F: NaClO oxidation (NaClO), 15 = G: UV oxidation(UV))																									
4	116.0	-	*1*		-	19.7	-	*1*		-	15.5	-	*1*		-	11.1	-	*1*		-	-	-	-		-
8	-	-	-		-	-	-	-		-	3.0	-	*1*		-	6.1	-	*1*		-	-	-	-		-
15	54.0	-	*1*		-	14.8	-	*1*		-	10.4	-	*1*		-	4.7	-	*1*		-	0.0	-	*1*		-

[a] BC = BC concentration in g kg^{-1}

[b] s = standard deviation

[c] n = number of replicates

[d] u = standard uncertainty

[e] CV = Coefficient of variation

[f] 10 = Team 10 did not assign any uncertainty to the measurements since they were not confident of the OC/BC split

Table 2. Black carbon concentrations of the BC-rich materials for individual teams, grouped according to method employed (g kg^{-1} mass). Bold type numbers are over all the teams in the method.

Lab	Soot					Wood char					Grass char				
	BC	*s*	*n*	*u*	*CV*	BC	*s*	*n*	*u*	*CV*	BC	*s*	*n*	*u*	*CV*
A. Thermal oxidation method (CTO-375)															
1	439.6	*53.4*	*6*	*21.8*	*12.1*	0.0	-	*5*		-	21.0	*5.1*	*6*	*2.1*	*24.3*
5	*325* [g]	*164.0*	*3*	*94.7*	*50.0*	0.0	-	*3*		-	6.4	*2.3*	*3*	*1.3*	*35.9*
7a	428.0	*19.0*	*3*	*11.0*	*4.4*	0.0	-	*3*		-	2.5	*0.2*	*3*	*0.1*	*8.0*
7b	-	-	-		-	-	-	-		-	-	-	-		-
12a	422.1	*15.1*	*2*	*10.7*	*3.6*	0.0	-	*1*		-	5.1	*0.0*	*2*	*0.0*	*0.0*
12b	437.8	*22.7*	*3*	*13.1*	*5.2*	0.0	-	*1*		-	9.9	*0.1*	*1*	*0.1*	*1.0*
Average	**431.9**					**0.0**					**9.0**				
n	**5**					**5**					**5**				
s	**8.3**										**7.2**				
B. Molecular markers method (BPCA)															
2	160.9	*25.9*	*2*	*18.3*	*16.1*	250.6	*64.3*	*2*	*45.5*	*25.7*	175.7	*46.0*	*3*	*26.6*	*26.2*
6	474.2	*57.0*	*3*	*32.9*	*12.0*	226.1	*57.7*	*2*	*40.8*	*25.5*	145.7	*32.9*	*2*	*23.2*	*22.6*
14	83.48	*10*	*3*	*5.5*	*11.5*	72.92	*6.4*	*3*	*3.7*	*8.8*	142.5	*37.5*	*3*	*21.7*	*26.3*
Average	**239.5**					**183.2**					**154.6**				
n	**3**					**3**					**3**				
s	**206.9**					**96.3**					**18.3**				
C. Acid dichromate oxidation (Cr_2O_7)															
11	400.7	*1.8*	*2*	*1.3*	*0.4*	560.1	*0.0*	*2*	*0.0*	*0.0*	149.6	*1.4*	*2*	*1.0*	*0.9*
13	-	-	-		-	545.7	*156*	*8*	*55.2*	*28.6*	200.5	*70.6*	*8*	*25.0*	*35.2*
16b	539.0	*38.9*	*3*	*22.5*	*7.2*	371.7	*17.4*	*3*	*10.0*	*4.7*	203.2	*10.8*	*3*	*6.2*	*5.3*
17	-	-	-		-	620.0	-	*1*		-	270.0	-	*1*		-
Average	**469.9**					**524.4**					**205.8**				
n	**2**					**4**					**4**				
s	**97.8**					**106.7**					**49.4**				

Table 2 (continued). Black carbon concentrations of the BC-rich materials for individual teams, grouped according to method employed (g kg^{-1} mass). Bold type numbers are over all the teams in the method.

Lab	Soot					Wood char					Grass char				
	BC	*s*	*n*	*u*	*CV*	BC	*s*	*n*	*u*	*CV*	BC	*s*	*n*	*u*	*CV*
D. Thermal/optical reflectance and transmittance method (TOT/R)															
3	904.1	*41.3*	*3*	*23.8*	*4.6*	679.0	*5.9*	*3*	*3.4*	*0.9*	388.3	*13.1*	*3*	*7.6*	*3.4*
9a	867.1	*8.0*	*3*	*4.6*	*0.9*	731.7	*6.7*	*3*	*3.9*	*0.9*	537.7	*10.4*	*3*	*6.0*	*1.9*
9b	865.5	*9.0*	*3*	*5.2*	*1.0*	731.4	*7.3*	*3*	*4.2*	*1.0*	575.2	*8.6*	*3*	*5.0*	*1.5*
[f]10	880.0	-	*3*		-	610.0	-	*3*		-	500.0	-	*3*		-
16a	921.2	*16.4*	*3*	*9.5*	*1.8*	511.3	*5.1*	*3*	*2.9*	*1.0*	433.7	*2.3*	*3*	*1.3*	*0.5*
Average	**887.6**					**652.7**					**487.0**				
n	**5**					**5**					**5**				
s	**24.3**					**93.5**					**76.0**				
CV	**3**					**14**					**16**				
Other independent methods (4 = E: Thermogravimetry (TG-DSC), 8 = F: NaClO oxidation (NaClO), 15 = G: UV oxidation(UV))															
4	841.5	-	*1*		-	709.5	-	*1*		-	344.2	-	*1*		-
8	641.3	*16.2*	*3*	*9.4*	*2.5*	0.0	-	*3*		-	62.5	*19.1*	*3*	*11.0*	*30.6*
15	788.9	-	*1*		-	705.2	-	*1*		-	454.2	-	*1*		-

[f]10 = Team 10 did not assign any uncertainty to the measurements since they were not confident of the OC/BC split

Table 3. Black carbon concentrations of the potential interfering materials for individual teams, grouped according to method employed (g kg^{-1} mass). Bold type numbers are over all the teams in the method.

Lab	Melanoidin					Shale					Lignite coal					Bituminous coal				
	BC	*s*	*n*	*u*	*CV*	BC	*s*	*n*	*u*	*CV*	BC	*s*	*n*	*u*	*CV*	BC	*s*	*n*	*u*	*CV*
A. Thermal oxidation method (CTO-375)																				
1	12.9	*1.0*	*6*	*0.4*	*7.8*	1.7	*0.2*	*3*	*0.1*	*11.8*	10.4	*0.9*	*4*	*0.5*	*8.7*	19.3	*2.9*	*6*	*1.2*	*15.0*
5	0.7	*0.4*	*3*	*0.2*	*57.1*	29.9	*0.9*	*3*	*0.5*	*3.0*	3.7	*0.1*	*3*	*0.1*	*2.7*	5.9	*1.8*	*3*	*1.0*	*30.5*
7a	25.0	*2.2*	*3*	*1.3*	*8.8*	0.9	*0.0*	*3*	*0.0*	*0.0*	14.3	*0.4*	*3*	*0.2*	*2.8*	41.9	*0.5*	*3*	*0.3*	*1.2*
7b	-	-	-		-	-	-	-		-	-	-	-		-	-	-	-		-
12a	1.9	-	*1*		-	0.1	*0.0*	*2*	*0.0*	*0.0*	0.0	-	*1*		-	0.3	-	*1*		-
12b	25.5	-	*1*		-	0.6	-	*1*		-	2.1	-	*1*		-	15.4	-	*1*		-
Average	**13.2**					**6.6**					**6.1**					**16.6**				
n	**5**					**5**					**5**					**5**				
s	**12.0**					**13.0**					**6.0**					**16.0**				
B. Molecular markers method (BPCA)																				
2	5.8	*0.5*	*2*	*0.4*	*8.6*	10.7	*0.2*	*2*	*0.1*	*1.9*	60.1	*6.2*	*2*	*4.4*	*10.3*	139.0	*15.8*	*2*	*11.2*	*11.4*
6	4.7	*0.8*	*2*	*0.6*	*16.7*	-	-	-		-	-	-	-		-	-	-	-		-
14	4.5	*0.6*	*2*	*0.4*	*13.5*	17.4	-	*1*		-	170.7	*6.8*	*2*	*4.8*	*4.0*	222.7	*30.2*	*2*	*21.4*	*13.6*
Average	**5.0**					**14.1**					**115.4**					**180.8**				
n	**3**					**2**					**2**					**2**				
s	**0.7**					**4.8**					**78.2**					**59.1**				
C. Acid dichromate oxidation (Cr_2O_7)																				
11	0.0	*0.0*	*2*	*0.0*	-	41.2	*4.6*	*2*	*3.3*	*11.2*	69.8	*3.3*	*2*	*2.3*	*4.7*	655.8	*9.9*	*2*	*7.0*	*1.5*
13	0.0	-	*6*		-	-	-	-		-	-	-	-		-	-	-	-		-
16b	0.1	*0.0*	*3*	*0.0*	*0.0*	11.9	*1.0*	*3*	*0.6*	*8.4*	65.1	*3.5*	*3*	*2.0*	*5.4*	805.8	*39.9*	*3*	*23.0*	*5.0*
17	0.0	-	*1*		-	-	-	-		-	31.0	-	*1*		-	720.0	-	*1*		-
Average	**0.0**					**26.6**					**55.3**					**727.2**				
n	**4**					**2**					**3**					**3**				
s	**0.1**					**20.7**					**21.2**					**75.3**				

Table 3 (continued). Black carbon concentrations of the potential interfering materials for individual teams, grouped according to method employed (g kg^{-1} mass). Bold type numbers are over all the teams in the method.

Lab	Melanoidin					Shale					Lignite coal					Bituminous coal				
	BC	s	n	u	CV	BC	s	n	u	CV	BC	s	n	u	CV	BC	s	n	u	CV
D. Thermal/optical reflectance and transmittance method (TOT/R)																				
3	236.0	*41.7*	*3*	*24.1*	*17.7*	39.5	*1.7*	*3*	*1.0*	*4.3*	333.6	*65.7*	*3*	*37.9*	*19.7*	672.5	*30.4*	*3*	*17.6*	*4.5*
9a	370.8	*1.8*	*3*	*1.0*	*0.5*	25.5	*0.8*	*3*	*0.5*	*3.1*	326.2	*8.2*	*3*	*4.7*	*2.5*	733.2	*8.6*	*3*	*5.0*	*1.2*
9b	344.1	*16.0*	*3*	*9.2*	*4.6*	24.8	*0.5*	*3*	*0.3*	*2.0*	322.2	*8.4*	*3*	*4.8*	*2.6*	442.3	*44.1*	*3*	*25.5*	*10.0*
[f]10	86.0	-	*3*		-	0.0	-	*3*		-	-	-	-		-	-	-	-		-
16a	278.9	*0.4*	*3*	*0.2*	*0.1*	3.6	*0.9*	*3*	*0.5*	*25.0*	109.9	*0.2*	*3*	*0.1*	*0.2*	631.6	*1.8*	*3*		*0.3*
Average	**263.2**					**18.7**					**273.0**					**619.9**				
n	**5**					**5**					**4**					**4**				
s	**112.4**					**16.5**					**108.8**					**125.5**				
Other independent methods (4 = E: Thermogravimetry (TG-DSC), 8 = F: NaClO oxidation (NaClO), 15 = G: UV oxidation(UV))																				
4	2.7	-	*1*		-	17.4	-	*1*		-	112.0	-	*1*		-	782.3	-	*1*		-
8	0.0	-	*3*		-	-	-	-		-	29.8	*7.5*	*3*	*4.3*	*25.2*	-	-	-		-
15	0.0	-	*1*		-	15.8	-	*1*		-	196.3	-	*1*		-	859.0	-	*1*		-

[f]10 = Team 10 did not assign any uncertainty to the measurements since they were not confident of the OC/BC split

Centennial black carbon turnover observed in a Russian steppe soil

Karen Hammes[1], Margaret S. Torn[2], Andrei G. Lapenas[3] & Michael W.I. Schmidt[1,*]

[1] *University of Zurich, Department of Geography, University of Zurich, Winterthurerstrasse 190, CH-8057, Zurich, Switzerland*

[2] *Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA*

[3] *Deparment of Geography and Planning, University at Albany, NY 12222, USA*

* Corresponding author. Fax: +41 635 6841
E-mail: *Michael.schmidt@geo.unizh.ch*

Abstract

Black carbon (BC), from incomplete combustion of fuels and biomass, has been considered highly recalcitrant and a substantial sink for carbon dioxide. Recent studies have shown that BC can be degraded. We use soils sampled 100 years apart in a Russian steppe preserve to generate the first whole-profile estimate of BC stocks and turnover. BC stocks (initially stock 2.5 kg m^{-2}) decreased 25% with cessation of biomass burning. BC turnover in the soil was 293 y (best estimate; range 212-541 y), much faster than inert/passive carbon in soil models. Such results provide a new constraint on theories of soil carbon stabilization and atmospheric budgets. Most importantly, BC cannot be assumed chemically recalcitrant in all soils; other explanations for very old carbon are needed.

Introduction

Black carbon (BC) is a product of incomplete combustion of fossil fuels and biomass burning (Goldberg, 1985) and constitutes a significant, yet relatively poorly understood component of soil organic carbon. Black carbon has been considered a missing inert carbon sink of the terrestrial carbon cycle (Skjemstad et al., 1996; Kuhlbusch, 1998). Recent short-term laboratory and field studies have shown evidence for degradation of BC (Bird et al., 1999; Hamer et al., 2004; Masiello, 2004; Hockaday et al., 2006), but there has been no long-term *in situ* confirmation. We took advantage of a 100-year interval soil sampling of a Russian Chernozem to study long-term change of BC in the field.

Chernozems cover more than 230 million ha worldwide (FAO, 2001), and almost 100 million ha in Russia alone (Stolbovol, 1998). Russian Chernozems have substantial organic carbon stocks, of 28-34 kg m^{-2} for the top 1 m under native grassland (Mikhailova & Post, 2006).

Experimental section

Site climate

The mean annual temperature from 1989-1998 was 6.6 °C, which is 1.3 °C warmer than the mean annual temperature from 1893-1950 (5.3 °C). The total annual rainfall from 1989-1998 was 507.7 mm, which is an increase of 70 mm (mostly winter precipitation) from the period 1893-1950 (438.5 mm; Stolbovol, 1998). Additional information on the climate conditions in the area can be found at: http://data.giss.nasa.gov/gistemp/station_data/ using the stations Kamennaja Ste (51° 0' N, 40° 7' E) and Voronez (51° 7' N, 39° 2' E).

Soil sampling

The Chernozem soils were sampled in a Russian steppe preserve, in the Kamennaya Steppe National Park (51° 0' N, 40° 7' E), created between 1882 and 1885. The 100-year old soil monolith was collected between 1895 and 1903 (called 1900 soil from here on) within the Dukachaev Institute located in the preserve, and is almost 140 cm long. According to the

original sampling notes and current observations, the monolith was sampled without disturbing the horizon structure, and kept horizontal without any resin treatment in a wood box to keep it dust-free. The location of the sampled site and the collection procedures were detailed previously (Lapenis et al., 2000; Torn et al., 2002). In August 1997, a soil profile was sampled from exactly the same location under the same land use. Soil organic carbon and carbon isotopes (^{13}C and ^{14}C) were compared in archived and modern profiles (Torn et al., 2002). An additional profile (0-100 cm) was sampled in 2004 in a second pristine steppe area in the same preserve. At about the same time as preserve establishment around 1900, almost all of the region's steppe was converted to agriculture and, most importantly for our study, fires which were frequent on the steppe, were suppressed by human activity, resulting in almost total cessation of once frequent biomass burning inputs of BC to soil. These circumstances gave us the unique opportunity to study the response of BC stocks over a long time period *in situ*, and without land use change, and to estimate a turnover rate of the BC in the soil.

An additional profile was sampled in August 2004 in a second pristine steppe area in the same preserve. It was roughly 1 km from the 1900 pit and 1997 site 1 (analysed here for BC), and within 50 m of the 1997 site 2 (analysed with the 1900 and site 1 samples for C, ^{13}C and ^{14}C), all four of which are located in the same preserve and under the same steppe land cover. This soil was sampled to a depth of 100 cm after scraping away the open wall of an existing soil pit. Samples were collected from the wall of the pit, starting from the bottom and sampling in a channel over the whole of each horizon. The sampling increments for this soil profile were not the same as for the 1900 and 1997 soils and thus profile totals may be compared but discrete depth increments are not comparable.

Black carbon analysis

We analysed BC in each soil horizon using benzene polycarboxylic acid (BPCA) as markers for the presence of fire-derived organic matter (Brodowski et al., 2005). Briefly, triplicate samples were digested with HNO_3 at 170 °C for eight hours, purified, and the BPCA in each sample analysed after derivatisation on a gas chromatograph equipped with a flame ionization detector. We deviated from the original method, by using phthalic acid as internal standard instead of citric acid. The error bars for each point on the graphs are the standard errors of two to three single digestion analyses.

Statistics

A one-tailed t-test with matched pairs was done to test the hypothesis that the 1997-soil does not have less BC than the archive soil (JMP 5.1.2, SAS).

Model parameters

The turnover time of BC was modelled with the following equation:

$$\tau = -t/\ln(f-b/(f-1)$$

where τ = turnover time (years); t = time between samplings (years); f = ratio of modern BC input flux to historic input flux; b = fraction of original BC stock remaining. For this model we made three assumptions: (1) BC is homogenous with respect to turnover, (2) loss of BC from the soil is a first order decay process, i.e. the loss of BC per unit time is proportional to the BC stock, and (3) after the 1900 sampling, BC inputs decreased in accord with the decrease in regional fire frequency (Torn et al., 2002).

Model sensitivity analysis

The archive soil was sampled somewhere between 1898 and 1903, which gives a six year variation on the 100-year period to 1997, i.e. t (time between samplings, years) could be from 102 years (maximum difference) to 94 years (minimum difference). Thus, we chose t=102 and t=94 years to test model sensitivity with. Since there have been climatic changes in the region, it could be that the bulk density of the soil had changed over the 100 year period. We varied the bulk density from -10% change (less dense) to +10% change (denser) from the measured bulk density of 1997 (Torn et al., 2002). These bulk density values (0.9 to 1.1) were multiplied with b (fraction of original BC stock remaining), b=1.92 kg m^{-2}/2.55 kg m^{-2} to give an estimate of the fraction of BC remaining with different bulk density values. The fire frequency in the region has decreased, and thus so has the BC input to the soil. Since we cannot quantify the reduction in BC input, we chose two input levels (f): f=0, where there has been no BC input for 100 years and f=0.1, assuming a 90% reduction in BC input.

Results

Black carbon concentrations

The 1997 BC concentrations are significantly lower than the 1900 BC concentrations throughout the soil (P=0.015), and follow the same trend down the profile, decreasing with depth to almost zero at around 120-130 cm (Fig. 1A). Few other studies to date have quantified BC concentrations over the whole soil profile (Kleber et al., 2003; Wang et al., 2005; Rodionov et al., 2006). Most BC concentration studies report only the topsoil (up to 30 cm depth) values. However, the actual peak concentration of BC is below the topsoil. BC makes up 7% of OC in the whole profile in these soils, with a peak concentration (peak contribution to OC) of about 10% at 30-50 cm (Fig. 1B). The 2004 BC concentrations also decrease with depth, but this soil has its maximum concentration nearer to the surface (5-20 cm, Fig. 1A). BPCA data are sometimes multiplied with a conversion factor of 2.27 to compensate for incomplete BC recovery (Brodowski et al., 2005). However, this factor is currently disputed. Studies limited to surface horizons miss the location of most concentrated BC, and where BC contributes most to soil organic C. Analyzing BC with the same method, another study on Russian Chernozems further north (Kursk) also found the maximum BC concentration between 30 and 50 cm (49-75 g BC kg^{-1} C, with the conversion factor, 22-33 g BC kg^{-1} without) (Rodionov et al., 2006). This study did not report BC stocks or bulk density, and also almost no studies in other areas have either, making it almost impossible to determine storage and BC turnover rates in soils (Preston & Schmidt, 2006).

Black carbon stock

The profile-total black carbon stocks of the 1997 and 2004 - soils are 25% lower than that of the 1900 soil (1.9 kg C m^{-2} and 2.0 kg C m^{-2} vs. 2.0 kg C m^{-2} respectively) (inset to Fig. 1C). In calculating BC stock values, we used bulk densities from Torn et al. (2002), in soil profiles sampled in 1997 in the locations of the 1900, 1997, and 2004-soil collections. Our results suggest that BC was lost from the soil over 100 years. Other studies, summarised by Forbes et al. (2006), suggest substantial losses of BC in other soils in hundreds of years. While the BC stocks for the 1900 and 1997 soils are similar in the top 20 cm, in the 40-80 cm region the 1997 soil has a consistently lower BC stocks than the historic, 1900 soil (Fig. 1C and inset to Fig. 1C). Data on soil BC stocks worldwide are scarce (Preston & Schmidt, 2006) and no data were found on other Russian Chernozems. BC stock (using the same quantification method) in a German Chernozem was similar to our site, with 2.3 kg m^{-2} to 1 m depth, with larger BC stock in the subsoil than in the topsoil (Kleber et al., 2003). Comparative data (using the same quantification method) are available for a German chernozemic soil (up to 1 m depth) where a BC stock of 2.3 kg m^{-2} was calculated (the largest BC stock was found in the subsoil compared to the topsoil) (Kleber et al., 2003). For comparison with our surface BC stocks (values in Figure 1C) in the surface soil of a North American prairie, BC stocks were 0.1-1.5 kg m^{-2} for the top 10 cm (Glaser et al., 2003). In a study using a different BC quantification method (UV oxidation), BC stocks were 0.3-0.4 kg m^{-2} for the top 20 cm under mixed-grass savanna in Texas (Ansley et al., 2006). The BC stock in the top 5 cm of a savanna soil in Zimbabwe was 0.04 kg m^{-2} (using a dichromate oxidation method) (Bird et al., 1999). This study was done only for the top 5 cm of soil and over a shorter time period (in 1999 it was 50 years since burning stopped). The fact that stock values are usually only given for the top 10-20 cm, underestimates the black carbon and carbon stocks of these deep carbon-rich soils (Torn et al., 2002; Preston & Schmidt, 2006). The total carbon stocks and sink or source potential in these soils is much larger than conveyed by only considering the topsoil.

Black carbon turnover modelling

Having BC stock at two points in time allowed us to estimate the turnover time of the BC using the stock values in a simple model (Fig. 2).

We calculate the maximum turnover time of BC in this soil to be between 444 and 541 years, and the minimum being 212-262 years, with the ranges varying with assumptions about sampling interval, fire cessation, and bulk density as described in Methods.

The conservative maximum turnover time of 541 years is calculated assuming post-1900 inputs of BC were reduced completely, bulk density has increased by 10% and the soil was sampled in the earliest year mentioned (1895; t=102 y).

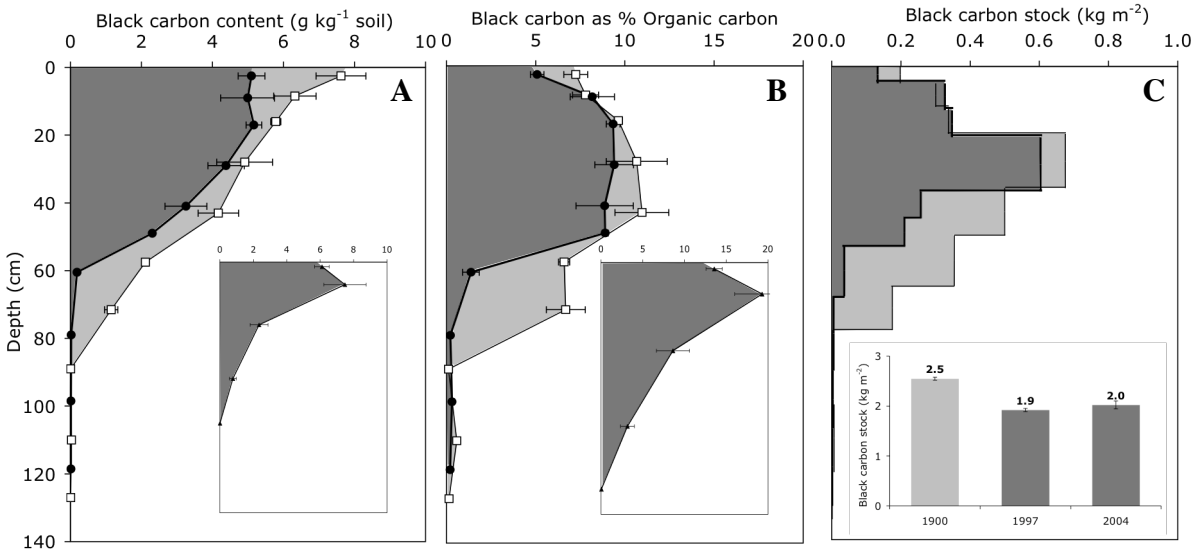

Fig. 1. (**A**) Black carbon concentrations of the 1900 soil (thin black line, open squares), 1997 soil (thick black line, filled circles) compared to a nearby Chernozem sampled in 2004 (inset). The data are without the 2.27 correction factor often used with the BPCA method to compensate for the fact that not all BC is converted to BPCA (Brodowski et al., 2005). Error bars are standard errors (n=2-3). (**B**) Black carbon as proportion of organic carbon for the 1900 soil, 1997 soil and comparative 2004 soil (inset). (**C**) Black carbon stock of the 1900 and 1997 soils (2004 soil only shown as profile total). Inset to Figure 1C shows that also total profile BC stocks decreased 25% between 1900 and 1997. The comparative 2004 soil is also about 25% lower.

Our best estimate, calculated with previously published sampling date (1903), and bulk density (no change from present), and the assumption of a 90% reduction in pre-1900 BC inputs from biomass burning, is 293 y. The tropical Zimbabwe soil mentioned earlier (4) had a turnover time between 50 and 100 years, which is faster than ours, but was estimated only for 0-5 cm and in a warm, tropical climate.

Discussion

Black carbon with ages >1000 years, has been found preserved in soil, suggesting a long turnover time (millennia) in some cases (Forbes et al., 2006), but like all soil organic matter, BC exists in a continuum of turnover times. If all BC had such long turnover times there would be much more BC present in the soil. The majority of BC is thought to be either consumed in subsequent fires (Preston & Schmidt, 2006) or lost through other mechanisms when fire is suppressed (Forbes et al., 2006). The rate of this BC turnover is a function of its formation conditions (e.g. fire temperature, duration and oxygen supply) (Baldock & Smernik, 2002; Brodowski et al., 2006; Cheng et al., 2006), and the environment (e.g. climate, soil aggregation, mineralogy, biological activity) (Masiello, 2004). Variations in formation conditions and the environment support the idea of BC as a continuum of more or less condensed elemental carbon with different chemical and physical reactivity (Preston & Schmidt, 2006). Oxidised BC has been found in dissolved organic matter in a forest soil with visible pieces of 100-year-old charcoal in the topsoil, where filamentous bacteria was seen growing (Hockaday et al., 2006). Black carbon particles, deposited about 6000 years ago and collected from a tropical subsoil, displayed a highly aromatic core, and a highly functionalised (carboxylic and phenolic groups) outer surface where microbial and chemical degradation have taken place (Lehmann et al., 2005). Incubation studies show that BC stimulates the growth of microorganisms, providing more growth surfaces, which in turn break down the BC. With the addition of glucose, BC mineralisation is further enhanced. Co-metabolism could thus be an important mechanism of BC decay (Hamer et al., 2004). Bird et al. (1999) found that BC can undergo natural degradation, but could only speculate as to the mechanisms: oxidation to CO_2, illuviation to deeper parts of

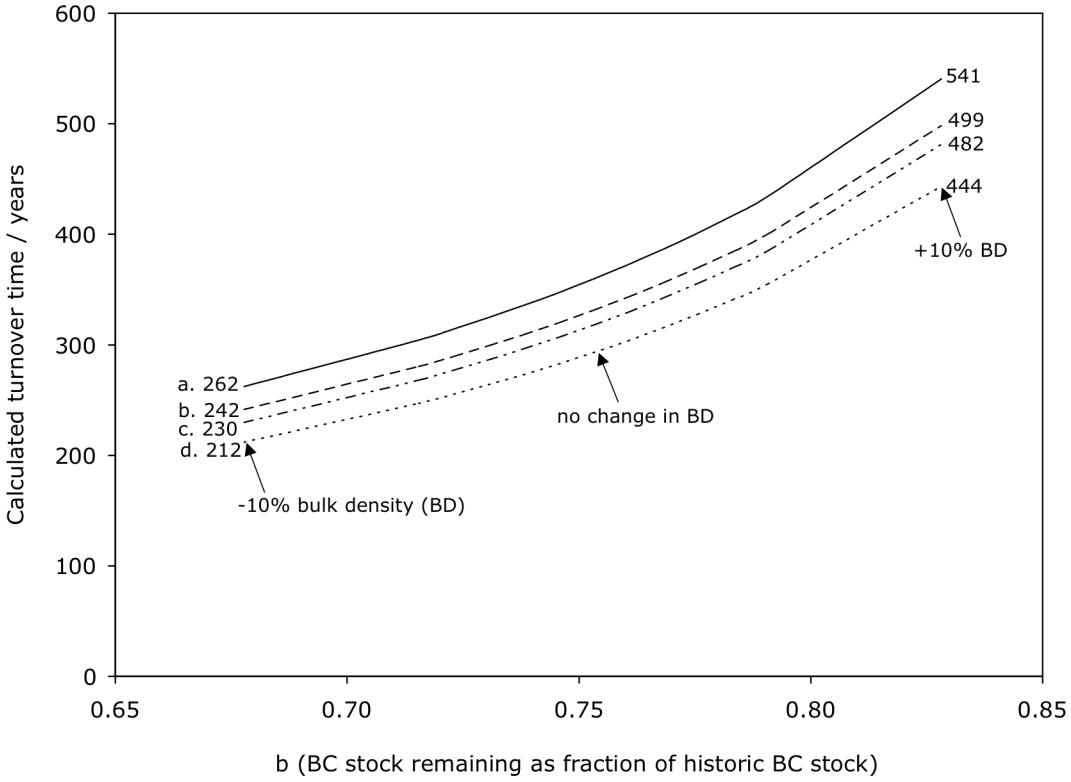

Fig. 2. Estimated turnover times in years for black carbon in the Russian steppe soil, using different uncertainties: a. (solid line) 100% reduction in BC inputs (f=0), monolith 102 years old (t=102 years); b. 90% reduction in BC inputs (f=0.1), monolith 102 years old (t=102 years); c. 100% reduction in BC inputs (f=0), monolith 94 years old (t=94 years); and d. (dotted line) 90% reduction in BC inputs (f=0.1), monolith 94 years old (t=94 years). The minimum and maximum turnover times for each model uncertainty is indicated on the left- and right-hand side of the lines, respectively.

the soil profile, or solubilisation and loss as dissolved organic matter.

There has been an increasing trend in precipitation and temperature since the 1950's in our study area (Sentsova, 2002), which could have altered the decomposition rate of the soil organic matter by increasing soil moisture and chemical and microbial activity. The influence of environmental conditions on BC degradation is not well known, but warming can enhance decomposition even of relatively recalcitrant organic matter (Knorr et al., 2005). Thus it is possible that these climatic trends have accelerated BC degradation in this region relative to their rates before 1950. In this case, our estimated turnover time is possibly slower than expected for the current climatic conditions, since the period around the turn of the previous century had a less favourable climate for decomposition in this region.

Black carbon in this soil turns over on a 212-541 y time scale, which is much faster than previously thought (IPCC, 2001). Estimates of the residence time of BC in soil, such as those presented here, can provide a new and important constraint on atmospheric black (elemental) carbon budgets, by allowing long-term BC deposition rates to be estimated from current soil stocks. Moreover, this BC turns over more rapidly than the bulk organic matter at this site (Torn et al., 2002), meaning that it is more labile than other constituents. There has been a search for the source or underlying mechanisms of stable soil organic carbon (SOC), intrinsic chemical recalcitrance being one type. Our results on BC turnover appear to remove one of the last potential candidates for chemically recalcitrant carbon inputs, termed passive or intert in soil organic matter models. There is, however, evidence that BC together

with other SOC compounds can be very stable when stabilised in microaggregates (<250 μm) and bound in organo-mineral complexes (e.g. with iron oxides) and clay minerals in the soil where it is protected from fast degradation (Torn et al., 2002; Golchin et al., 1997; Esterhues et al., 2005; Brodowski et al., 2006). An improved understanding of the mineral controls on BC and OC turnover is needed to better quantify the role that soil can play in sequestrating carbon or generating feedback that amplifies climate change.

Acknowledgements

This work was partially supported by the Office of Science, U.S. Department of Energy under Contract No. DE-AC02-05CH11231. Andrei Lapenas was funded by the NSF Ecosystem Studies Program and Karen Hammes by the University of Zurich and the Lawrence Berkeley National Laboratory.

References

Ansley, R.J., Boutton, T.W., Skjemstad, J.O. (2006) Soil organic carbon and black carbon storage and dynamics under different fire regimes in temperate mixed-grass savanna. Global Biogeochemical Cycles 20, GB3006, doi:10.1029/2005GB002670.

Baldock, J.A., Smernik, R.J. (2002) Chemical composition and bioavailability of thermally altered *Pinus resinosa* (Red pine) wood. Organic Geochemistry 33, 1093-1109.

Bird, M.I., Moyo, C., Veenendal, E.M., Lloyd, J., Frost, P. (1999) Stability of elemental carbon in a savanna soil. Global Biogeochemical Cycles 13(4), 923-932.

Brodowski, S., Rodionov, A., Haumaier, L., Glaser, B., Amelung, W. (2005) Revised black carbon assessment using benzene polycarboxylic acids. Organic Geochemistry 36, 1299-1310.

Brodowski, S., John, B., Flessa, H., Amelung, W. (2006) Aggregate-occluded black carbon in soil. European Journal of Soil Science 57, 539-546.

Cheng, C.-H., Lehmann, J., Thies, J.E., Burton, S.D., Engelhard, M.H. (2006) Oxidation of black carbon by biotic and abiotic processes. Organic Geochemistry 37(11), 1477-1488.

Esterhues, K., Rumpel, C., Kögel-Knabner, I. (2005) Stabilization of soil organic matter isolated via oxidative degradation. Organic Geochemistry 36, 1567-1575.

Forbes, M.S., Raison, R.J., Skjemstad, J.O. (2006) Formation, transformation and transport of black carbon (charcoal) in terrestrial and aquatic ecosystems. Science of the Total Environment 370, 190-206.

Glaser, B., Amelung, W. (2003) Pyrogenic carbon in native grassland soils along a climosequence in North America. Global Biogeochemical Cycles 17(2), 1064, doi:10.1029/2002GB002019.

Golchin, A., Baldock, J.A., Clarke, P., Higashi, T., Oades, J.M. (1997) The effects of vegetation and burning on the chemical composition of soil organic matter of a volcanic ash soil as shown by ^{13}C NMR spectroscopy. II. Density fractions. Geoderma 76, 175-192.

Goldberg, E.D. *Black carbon in the environment* (John Wiley & Sons, Inc., New York, 1985).

Hamer, U., Marschner, B., Brodowski, S., Amelung, W. (2004) Interactive priming of black carbon and glucose mineralization. Organic Geochemistry 35, 823-830.

Hockaday, W.C., Grannas, A.M., Kim, S., Hatcher, P.G. (2006) Direct molecular evidence for the degradation and mobility of black carbon in soils from ultrahigh-resolution mass spectral analysis of dissolved organic matter from a fire-impacted forest soil. Organic Geochemistry 37, 501-510.

Intergovernmental Panel on Climate Change (IPCC), Climate Change 2001: The Scientific Basis. J.T. Houghton et al., Eds. (Cambridge Univ. Press, New York, 2001).

Knorr, W., Prentice, I.C., House, J.I., Holland, E.A. (2005) Long-term sensitivity of soil carbon turnover to warming. Nature 433, 2998-301.

Kuhlbusch, T.A.J. (1998) Black carbon and the carbon cycle. Science 280, 1903-1904.

Lapenis, A.G., Torn, M.S., Harden, J.W., Hollocker, K., Babikov, B.V., Timofeev, A.I., Hornberger, M.I., Nattis, R. (2000) Scientists unearth clues to soil contamination by comparing old and new soil samples. EOS Transactions AGU 81(6), 53, 59-60.

Lecture notes on the major soils of the world. (Eds. Driessen, P., Deckers, J., Spaargaren, O., Nachtergaele, F.) p. 227-231 (Food and Agricultural Organization of the United Nations, Rome, 2001).

Lehmann, J., Liang, B., Solomon, D., Lerotic, M., Luizão, F., Kinyangi, J., Schäfer, T., Wirick, S., Jacobsen, C. (2005) Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy for mapping nano-scale distribution of organic carbon forms in soil: Application to black carbon particles. Global Biogeochemical Cycles 19, GB1013, doi:10.1029/2004GB002435.

Masiello, C.A. (2004) New directions in black carbon organic geochemistry. Marine Chemistry 92, 201-213.

Mikhailova, E.A., Post, C.J. (2006) Organic carbon stocks in the Russian Chernozem. European Journal of Soil Science 57, 330-336.

Preston, C.M., Schmidt, M.W.I. (2006) Black (pyrogenic) carbon: a synthesis of current knowledge and uncertainties with special consideration of boreal regions. Biogeosciences 3, 397-420.

Rodionov, A., Amelung, W., Haumaier, L., Urusevskaja, I., Zech, W. (2006) Black carbon in the zonal steppe soils of Russia. Journal of Plant Nutrition and Soil Science 169, 363-369.

Schmidt, M.W.I., Skjemstad, J.O., Jäger, C. (2002) Carbon isotope geochemistry and nanomorphology of soil black carbon: Black chernozemic soils in central Europe originate from ancient biomass burning. Global Biogeochemical Cycles 16(4), 1123, doi:10.1029/2002GB001939.

Sentsova, N.I. (2002) Spatial and temporal variations in the formation of the Kamennaya steppe water regime. Water Resources 29, 622-625.

Skjemstad, J.O., Clarke, P., Taylor, J.A., Oades, J.M., McClure, S.G. (1996) The chemistry and nature of protected carbon in soil. Australian Journal of Soil Research 34, 251-277.

Stolbovol, V. (1998) Soils of Russia – Correlated with the revised legend of the FAO soil map of the world. International Institute for Applied Systems Analysis, Austria. Interim Report IR-98-037/December.

Torn, M.S., Lapenis, A.G., Timofeev, A., Fischer, M.L., Babikov, B.V., Harden, J.W. (2002) Organic carbon and carbon isotopes in modern and 100-year-old-soil archives of the Russian steppe. Global Change Biology 8, 941-953.

Wang, X., Peng, P.A., Ding, Z.L. (2005) Black carbon records in Chinese Loess Plateau over the last two glacial cycles and implications for paleofires. Palaeogeography, Palaeoclimatology, Palaeoecology 223, 9-19.

Curriculum vitae

Personal information

Last name	HAMMES
First name	Karen
Date of birth	18 December 1976
Nationality	South African

Education

Potchefstroom University, Potchefstroom, South Africa (1995-1997) (now University of North-West)
Faculty of Natural Sciences
B.Sc (Soil Science) – received March 1998

Pretoria University, Pretoria, South Africa (1998-1999)
Faculty of Natural and Biological Sciences
B.Sc. Hons. (Soil Science & Plant Production) – received April 2000

Pretoria University, Pretoria, South Africa (2000-2001)
Faculty of Natural and Biological Sciences
M.Sc. (Soil Science & Plant Production) – received March 2001
Thesis title: Nitrogen transformations in South African soils

University of Zurich, Zurich, Switzerland (2003-2007)
Faculty of Science
PhD (Physical Geography)
Thesis title: Analysis and fate of combustion residues in soil

Work Experience

Junior scientist (2000-2003)
Agricultural Research Council – Institute for Soil, Climate & Water, Pretoria, South Africa

PhD student/assistant (2003-2007)
Department of Geography, University of Zurich, Switzerland